One of the promising applications of nickel hydroxide is electrochemical electrochromic devices. To significantly improve the characteristics, the role of polyvinyl alcohol (PVA) in the synthesis and structure of composite $Ni(OH)_2$-PVA films was investigated by studying the effect of its concentration (30, 40, 50 g/l) and polymerization degree (17-99, 24-99, 30-99 types). Adhesion was investigated visually, and electrochemical and electrochromic properties – by cyclic voltammetry with simultaneous recording of optical characteristics. It was shown that at a concentration of 30 g/l, the film peeled off and had weak electrochemical and electrochromic properties. The presence of two cathodic peaks (E=500–510 mV and E=560 mV) on the cyclic voltammetry showed the presence of nickel hydroxide in the PVA matrix and nickel hydroxide with adsorbed PVA. This indicates the dual role of PVA as a surfactant and as a template. At low concentrations, the role of PVA as a surfactant prevailed. Increasing the concentration led to an increase in the film characteristics by strengthening the role of PVA as a template: at 50 g/l, the film did not peel off and has good electrochemical and electrochromic characteristics.

It is shown that at a low degree of polymerization, PVA (17-99 ype) mainly played the role of a surfactant but was also a template. The film cracked and had mediocre characteristics. The use of medium polymerization PVA (24-99 type) gave a film with high adhesion, electrochemical and electrochromic characteristics. It is shown that in this case, PVA performed the function of a template, there was only one cathodic peak on the voltammogram at E=500–510 mV. It was found that the use of PVA with a high degree of polymerization (30-99 type) led to a significant deterioration of the characteristics, including complete peeling of the film. This is probably due to the loss of PVA in the film

Keywords: nickel hydroxide, electrochromic film, polyvinyl alcohol, template, surfactant, degree of polymerization

DEFINITION OF THE ROLE OF POLYVINYL ALCOHOL DURING FORMATION AND IN THE STRUCTURE OF CATHODIC SYNTHESIZED COMPOSITE ELECTROCHROMIC NICKEL HYDROXIDE LAYER: TEMPLATE OR SURFACTANT

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1. Introduction

Nickel hydroxides are multifunctional substances [1]. They can be used as the basis of pigments [2]. Due to the high electrochemical activity, various forms of nickel hydroxide are used in chemical current sources (batteries [3] and supercapacitors [4, 5]). Because the oxidized form (NiOOH) has a brown-black color, and the reduced form ($Ni(OH)_2$) is

practically transparent, nickel hydroxide is used as an active substance in sensors [6] (similar to other electrochemical sensors [7]) and as electrochromic substance [8, 9].

From the point of view of the concept of sustainable development, electrochromic devices are a promising field of application for nickel hydroxide. With their help, significant savings can be made by reducing the cost of air conditioning with a significant increase in the comfort of living and working. The characteristics of electrochemical electrochromic devices are determined by the properties of the film of the electrochromic component, $Ni(OH)_2$.

To obtain thin transparent electrochromic films of nickel hydroxide, various methods can be used: chemical deposition [10, 11], homogeneous deposition [12], immersion method [13, 14], sol-gel method [15, 16], including the combination of methods [17], vacuum [18] and magnetic [19] sputtering, electrochemical deposition (colloidal and anodic [20], cathodic [21, 22], including Co doping [23] and cathodic deposition for use with non-aqueous Li-containing electrolyte [24]). Cathodic electrochemical deposition is very promising in terms of deposition technology.

However, the deposition of an electrochromic film from pure nickel hydroxide leads to significant degradation of the characteristics of the coating [25, 26], and, most importantly, to cracking and peeling of the film [27, 28]. To solve this problem, it is necessary to form an electrochromic layer of a composite material based on nickel hydroxide. Therefore, the investigation of the characteristics of such materials and the determination of the role of the components are relevant.

2. Literature review and problem statement

Composite materials can be divided into two broad types. The first one is a "matrix-filler" type described as a system where one of the components is a continuous (mainly polymeric) matrix, and the second component is a filler that changes (improves) the properties of the material [29]. The second type of a composite is a "main component-binder" described as a system consisting of the main discrete (often powder) component, connected into a single material by a binder component [30].

For a nickel hydroxide film, the particles of which must have electric contact with a conductive substrate with good adhesion to this substrate, the formation of a composite is possible only at the moment of layer formation. It should be noted that cracking and peeling of the $Ni(OH)_2$ layer occurs because the freshly formed hydroxide is a closed-cell system containing a very large amount of mother liquor. When dried, water evaporates and the volume of hydroxide decreases dramatically. Therefore, to prevent cracking and peeling, it is necessary to increase the plasticity of the hydroxide layer, which can only be achieved by introducing polymers. It was shown in [31] that the use of low-molecular-weight surfactants and classical water-insoluble binders (PTFE) did not solve the peeling problem. Therefore, high-molecular-weight materials must be used to form a composite coating. The formation of a composite of the "base substance-binder" type is possible during electrochemical synthesis in the presence of surfactants [32]. With this surfactant synthesis, particles of the substance are first formed, on which the surfactant is adsorbed. A "matrix-filler" type composite can be obtained by electrochemical template synthesis [33]. For this type of synthesis, the template first forms a porous matrix, inside which particles of the main substance are formed. The use of template synthesis has significant advantages over synthesis with surfactants since during template synthesis, a more plastic layer with higher adhesion is formed.

Because the electrochemical synthesis of a nickel hydroxide film is carried out from an aqueous solution, a water-soluble high-molecular-weight substance, for example, polyvinylpyrrolidone, should be used as a template [34]. Polyvinyl alcohol (PVA) is the most promising substance for the template synthesis of an electrochromic nickel hydroxide layer.

Various grades of PVA are known, differing in degree of hydrolysis, crystallinity, molecular weight, and presence of impurities [35, 36]. It should be noted that the PVA grade largely determines the properties of the composite materials in which it is used. In this case, the PVA characteristics are determined by the conditions and method of synthesis. Solubility, hydrophilicity, and the ability to form hydrogen bonds in PVA significantly depend on the degree of hydrolysis [37]. It was found in [38] that the characteristics of PVA samples of the same grade may differ, which, in the opinion of the authors, is due to structural differences. It was demonstrated in [39] that the conditions and methods for the PVA synthesis change the properties of the fibers obtained from this polymer. The use of PVA of various grades for colloidal stabilization of membrane-bound and membrane-closed enzymes significantly changes their activity [40]. It was also found that the molecular weight and degree of hydrolysis of PVA significantly affect the bioavailability and solubility of drugs [41].

Polyvinyl alcohol was used as a template for the synthesis of thin-film or mesoporous alumina (as a porosity control substance) [42, 43], hydroxyapatite crystallites (together with dodecyl sulfate) [44], mesoporous MFI zeolite (as a secondary template) [45], nanosized MgO [46]. PVA was used to obtain 3D structured oxides and a hierarchical zeolite for use in catalysis [47], a polypyrrole (PP) matrix (for use in an ammonia gas sensor) [48]. In this case, a mixed PP-PVA matrix was formed. PVA was also successfully used to obtain nickel hydroxide (as a separate substance) by template electrochemical synthesis [49] and template homogeneous precipitation [50, 51] (including low- and high-temperature ones [52]).

In [31], it was proposed to use template synthesis with PVA to obtain a $Ni(OH)_2$ film with high electrochromic properties and adhesion to the substrate. Experiments were carried out to investigate the influence of the preparation modes (temperature [53], time [54], and pulse-type [55] formation) and composition of the electrolyte (template concentration [56] and effect of tungstate anion as an activator [57]). In the described works, highly active electrochromic films with good adhesion were synthesized. However, they used only one type of PVA, or the PVA type was not described at all. In [58], two grades of PVA were compared, but no generalization was made. The main limitation of research on the choice of the optimal type of PVA and its content was the lack of data on the role of PVA in the formation process (template or surfactant) and, accordingly, the type of nickel hydroxide composite film ("matrix-filler" or "main component-binder"). PVA manufacturers [59, 60] indicated that PVA had surfactant properties. At the same time, it was shown in [56] that PVA formed a 3D network in the electrolyte, acting as a template. Therefore, clarifying the PVA's role in the formation of the $Ni(OH)_2$ film structure is of key importance.

3. The aim and objectives of the study

This work aims to reveal the role of polyvinyl alcohol in the structure of the nickel hydroxide electrochromic layer and the process of its formation. This will allow targeted selection of the optimal type of PVA and its concentration in the electrolyte for synthesis.

To achieve the aim, the following objectives were set:

– to investigate the adhesion, electrochemical and electrochromic characteristics of $Ni(OH)_2$ films obtained at various concentrations of PVA in the synthesis electrolyte with a low degree of polymerization;

– to investigate the adhesion, electrochemical and electrochromic characteristics of $Ni(OH)_2$ films obtained at different polymerization degrees of PVA.

4. Research materials and methods

4. 1. Materials and method for obtaining samples

Nickel nitrate hexahydrate (analytical grade qualification) was used for the synthesis. To determine the PVA role, the following PVA types were selected: 17-99, 24-99, and 30-99. If the PVA formula is represented as $(CH_2CHOH)_n(CH_2CHOOCCH_3)_m$, then n can be described as the number of hydroxyl groups (or chain units with a hydroxy group), and m – as the number of residual acetate groups (or chain units with an acetate group). According to manufacturers' data [59, 60], the second number (99) in the PVA type marking is the degree of hydrolysis calculated by the formula $n/(n+m)*100$. The first number (17 or 24 or 30) is described by PVA manufacturers as the degree of polymerization and is calculated using the formula $n+m$. Therefore, the first number in the PVA marking is directly proportional to the number of (-C-C-) segments in the carbon skeleton of the PVA polymer molecule and indicates the molecular weight of PVA. It should be noted that the samples of almost completely hydrolyzed PVA with different polymerization degrees (different molar masses) were used in the investigation.

The formation of samples of PVA-$Ni(OH)_2$ composite coatings was carried out on the surface of a transparent substrate – glass with a conductive layer of tin oxide doped with fluorine deposited on it (the so-called FTO glass). The investigation used commercial samples of FTO glass manufactured by Zhuhai Kaivo Optoelectronic Technology Co. Ltd. (China) with specific resistance $R<10$ Ohm/sq. The substrate was degreased with wet Na_2CO_3 paste, rinsed thoroughly, and sonicated (60 W, 41.5 kHz) in 96 % ethanol for 10 minutes. Before forming the coating, the base was dried. The working area of the FTO glass was 4 cm^2. The formation of an electrochromic $Ni(OH)_2$-PVA coating was carried out by cathodic template synthesis at a temperature of 30 °C, a cathodic current density of 0.1 mA/cm^2, and a deposition time of 10 minutes [31]. After synthesis, the FTO glass from the formed film was kept in distilled water for 10 minutes, after which it was dried at room temperature.

To investigate the effect of the polymerization degree of PVA, PVA 17-99, 24-99, or 30-99 were introduced into the electrolyte at the same concentration of 40 g/l. To determine the effect of concentration, PVA 17-99 with a low degree of polymerization was used at concentrations of 30, 40, and 50 g/l.

The marking of the obtained film samples is PVA-17-99-30, where PVA is the type of polymer in the composite film, 17 is the polymerization degree of PVA, 99 is the degree of PVA hydrolysis, and 30 is the PVA concentration in the synthesis electrolyte.

4. 2. Methods for investigating the samples

The electrochemical and electrochromic properties of the obtained samples were investigated by a complex method with simultaneous recording of a cyclic voltammogram (CV) and optical characteristics in a specially designed polymer cell. CV was carried out according to a three-electrode scheme: the working electrode was a $Ni(OH)_2$-PVA film sample on FTO glass; the counter electrode – a frame one, Ni foil; the reference electrode – saturated silver chloride; electrolyte – 0.1 M KOH. CV was carried out using an Elins R-8 electronic potentiostat (Russia) in the potential range [+201; +751 mV] relative to a normal hydrogen electrode (NHE) at a sweep rate of 1 mV/s. Optical properties (light transmission) were investigated using a specially designed circuit [31], and recording was performed using an E-154 ADC (Russia). The reduction or loss of the electrochromic properties of nickel hydroxide can be associated with either degradation of the electrochemical characteristics or peeling of the hydroxide film. Therefore, adhesion to the substrate and the presence of cracks or peeling of the coating were determined visually with photofixation immediately after electrochemical investigation.

5. Results of investigation of film characteristics at different concentrations and polymerization degrees of polyvinyl alcohol

5. 1. Results of investigation of film characteristics at different concentrations

The electrochemical and optical characteristics, as well as photographic images of the samples after CV, are shown in Fig. 1. It should be indicated from the photographic images that the adhesion to the base increased with increasing the PVA concentration: the PVA-17-99-30 sample completely exfoliated after cycling, the PVA-17-99-40 sample severely cracked and partially lost contact with the base, the PVA-17-99-50 sample mainly showed sufficient adhesion, but some peeling at the edges. The optical characteristics confirmed these data. The PVA-17-99-30 sample stopped coloring and bleaching after the second cycle. The PVA-17-99-40 sample was characterized by an insufficient coloring of the film (transparency in the colored state was 34 %), degradation occurred from cycle to cycle with an increase in transparency. The PVA-17-99-50 sample had higher optical characteristics (transparency in the colored state was 29 %), however, degradation was also observed. On the cyclic curves of the PVA-17-99-30 and PVA-17-99-40 samples, two cathodic peaks were found, a clearly pronounced one at $E=560$ mV and a wide one at $E=510-530$ mV. At the same time, only one peak was detected for the PVA-17-99-50 sample at $E=560$ mV, and the peak currents for this sample were higher than for the others. It should be noted that the cathodic peak currents decreased from cycle to cycle for all samples.

It was also found that the first anodic peak for all samples was clearly expressed and located at $E=700-710$ mV.
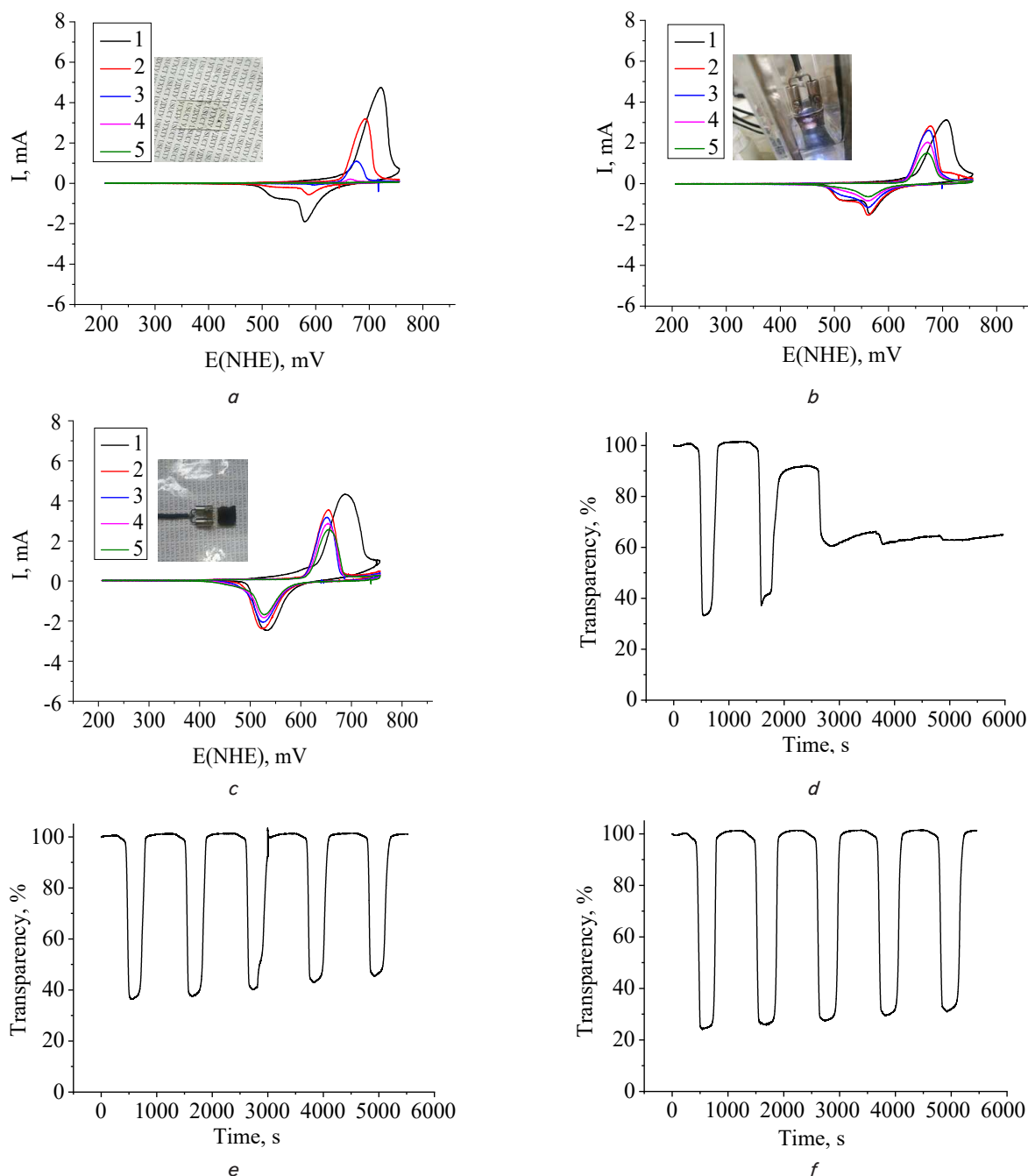
Fig. 1. Characteristics of samples obtained at different PVA concentrations:
a, b, c — voltammograms with photo images after cycling; *d, e, f* — optical characteristics; *a, d* — the PVA-17-99-30 sample;
b, e — the PVA-17-99-40 sample; *c, f* — the PVA-17-99-50 sample

5. 2. Results of investigation of film characteristics at different polymerization degrees

The electrochemical and optical characteristics, as well as photographic images of the samples after CV, are shown in Fig. 2. From the photographic images, it should be noted that at a concentration of 40 g/l, the best adhesion of the film was in the PVA-24-99-40 sample (medium degree of polymerization). At a low degree of polymerization (the PVA-17-99-40 sample), the film cracked, at a high degree of polymerization (the PVA-30-99-40 sample), the film peeled off. The optical characteristics confirmed these data. For the PVA-17-99-40 sample (low degree of polymerization), the transparency in the colored state was 34 %, with an increase in transparency from cycle to cycle. The PVA-17-99-50 sample (medium degree of polymerization)

had the highest optical characteristics, which were stable during cycling (transparency in the colored state was 27 %). On the cyclic curves of the PVA-17-99-40 samples (Fig. 1, *b*), two cathodic peaks were revealed, a clearly pronounced one at $E=560$ mV and a wide one at $E=510–530$ mV. The first anodic peak for this sample was clearly expressed and was located at $E=700–710$ mV. At the same time, only one peak was detected for the PVA-24-99-40 sample at $E=510–520$ mV, and the peak currents for this sample were the highest (5.3 mA in the second cycle). The first anodic peak was not expressed at all, its potential was probably higher than +750 mV. With an increase in the polymerization degree (the PVA-30-99-40 sample), the electrochemical characteristics deteriorated, and the cathodic peak currents sharply decreased.
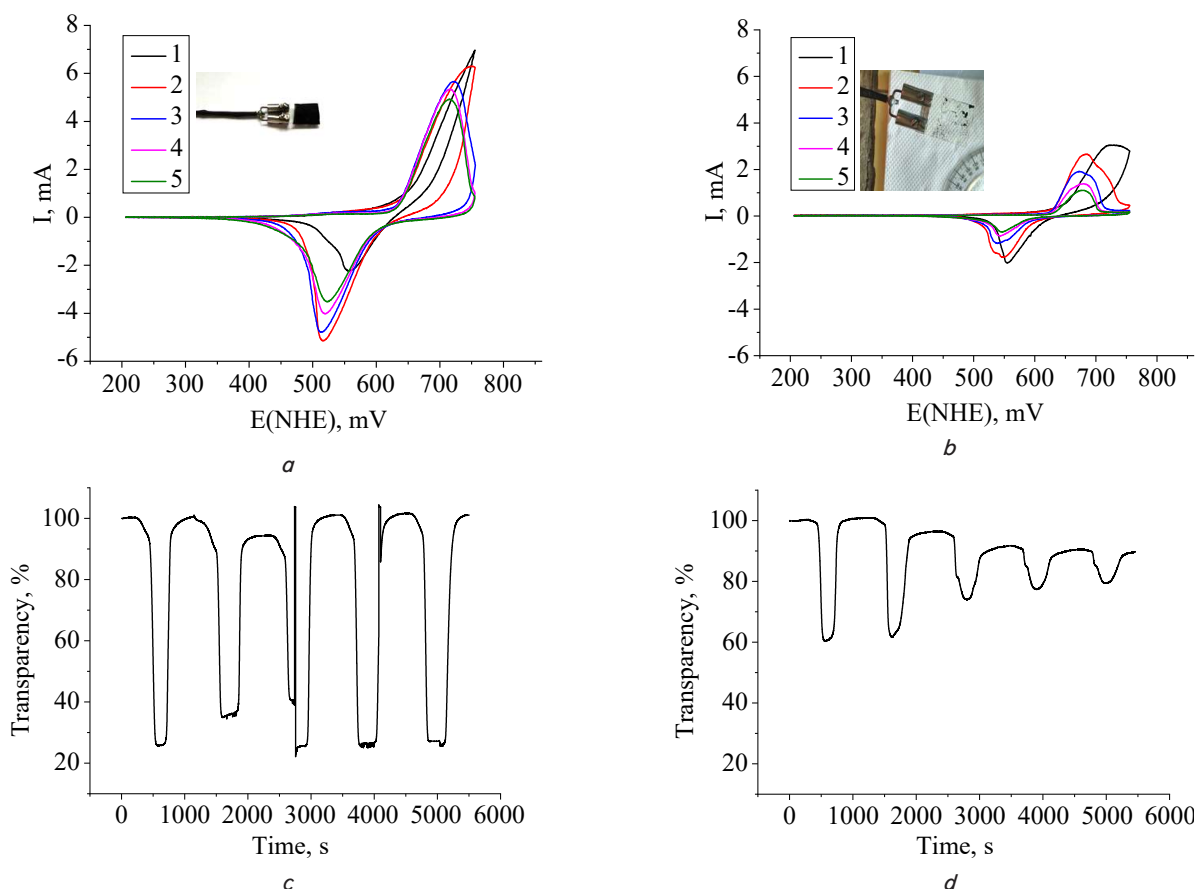
Fig. 2. Characteristics of the samples obtained at different polymerization degrees of PVA: *a, b* — voltammograms with photographic images after cycling; *c, d* — optical characteristics; *a, c* — the PVA-24-99-40 sample; *b, d* — the PVA-30-99-50 sample

In addition, a decrease in peak currents from cycle to cycle was revealed. The potential of the first cathodic peak was 560 mV.

6. Discussion of the investigation results at different concentrations and polymerization degrees of polyvinyl alcohol

When discussing the results, it is necessary to take into account the features of the template and surface-active action of polyvinyl alcohol. In the case of PVA acting as a surfactant, nickel hydroxide particles are first formed on the substrate surface, and PVA will be adsorbed on the surface of these particles. Thus, PVA will be concentrated closer to the outer edge of the layer. When the film dries, such an arrangement of PVA, whose molar mass is significantly higher than that of conventional surfactants, can lead to an increase in internal stresses and peeling of the film. In the case of acting as a template, when the base is placed in the electrolyte, PVA forms a 2D network on the surface of the base, in the cells of which particles of nickel hydroxide are formed. This should increase the plasticity of the film and its adhesion to the substrate.

Various concentrations of PVA. In this investigation, PVA with a low degree of polymerization was used (17-99). At a low concentration (the PVA-17-99-30 sample), the electrochromic coating film peels off already after the second cycle (Fig. 1, *d*). Increasing the concentration to 40 g/l (the PVA-17-99-40 sample) increases the adhesion and plasticity of the coating, however, the coating

cracks (Fig. 1, *b*), but the optical properties of the coating are not high. A further increase in the concentration to 50 g/l leads to the formation of a film with increased adhesion, however, partial delamination is observed along the edges of the sample (the PVA-17-99-50 sample). The optical and electrochemical properties of the sample are quite high, however, degradation of the characteristics is observed during cycling (a decrease in the peak currents on the CV and a decrease in the degree of coloring). During charge-discharge, the density of nickel hydroxide changes, and, accordingly, the volume of the particles. Therefore, the adsorption of large molecules on the surface of nickel hydroxide particles during cycling leads to film delamination. This effect is observed for the PVA-17-99-30 sample. At a low concentration, the amount of PVA (with a low degree of polymerization) is insufficient to form a complete template network. In this case, PVA mainly acts as a surfactant. The presence of two cathodic peaks on the voltammogram of the PVA-17-99-30 sample (Fig 1, *a*) (clearly pronounced at E=560 mV and broad at E=510–530 mV) indicates the presence of two different types of nickel hydroxide particles in the film. A clearly pronounced peak at E=560 mV corresponds to nickel hydroxide with the adsorbed PVA. Since nickel hydroxide in the template matrix interacts more strongly with PVA, a broad peak at E=510–530 mV corresponds to its type. Thus, the voltammogram clearly shows the dual role of PVA as a surfactant and as a template. The ratio of the cathodic peaks indicates a significantly greater role of PVA as a surfactant. Increasing the PVA concentration to 40 g/l improves film adhesion and optical characteristics. However, the voltammogram of the

PVA-17-99-40 sample also exhibits two cathodic peaks at the same potentials, which indicates that PVA retains the predominant role as a surfactant. However, when the concentration is increased to 50 g/l (the PVA-17-99-50 sample), the voltammogram (Fig. 1, *c*) shows one cathodic peak at E=560 mV, corresponding to nickel hydroxide in the PVA template. This indicates the predominant role of PVA as a template. A larger peak current indicates increased electrochemical activity. On the coloring-bleaching curve of this sample (Fig. 1, *f*), a higher coloration depth was revealed, which confirms the significantly higher efficiency of PVA as a template. Most likely, a concentration of 50 g/l is sufficient for the formation of a template matrix on the substrate surface.

Various polymerization degrees of PVA. Previously, in the PVA-17-99-40 sample (low degree of polymerization), the predominance of the PVA role as a surfactant was revealed. An increase in the polymerization degree (the PVA-24-99-40 sample) leads to a fundamental change in the characteristics. The adhesion of the film to the substrate is very high. The voltammogram of the sample (Fig. 2, *b*) revealed one cathodic peak at E=510−520 mV, corresponding to nickel hydroxide in the template matrix. In this case, the cathodic peak current (5.3 A) is significantly higher than the peak current of the PVA-17-99-40 sample (1.9 A), which indicates a high and stable electrochemical activity. In addition, the anodic peak of the first cycle is not pronounced, and the potential of the anodic peaks of the second and subsequent cycles is 750 mV (while for the PVA-17-99-40 sample, the first anodic peak is clearly pronounced at a potential of 700−710 mV). The coloration depth of this sample is also high (transparency in the colored state is 29 %), which indicates high electrochemical properties. All this indicates that in the PVA-24-99-40 sample, polyvinyl alcohol plays the role of a template during synthesis. A further increase in the polymerization degree of PVA to 30 (the PVA-30-99-40 sample) leads to a significant deterioration in the characteristics (Fig. 2, *c*, *f*). At a high degree of polymerization, PVA clearly forms the template matrix; however, at such a concentration, the amount of PVA in the film is excessive. This reduces the amount of nickel hydroxide in contact with the base, and, moreover, a part of PVA is sorbed on the already formed composite film. This causes the film to become heavier on the electrolyte side, resulting in delamination. The cathodic peak of the first cycle (Fig. 2, *c*) appears at a potential of 550 mV (typical for nickel hydroxide with adsorbed PVA). However, with further cycling, the potential of the cathodic peak shifts to values of 510−515 mV, which is typical for nickel hydroxide in the PVA matrix. It should be concluded that at a high

polymerization degree and concentration, PVA is primarily a template, forming a matrix. However, secondary adsorption of PVA then occurs, which worsens the characteristics.

The limitation of this investigation is the small number of PVA types investigated, which must be expanded to determine the optimal polymerization degree and concentration in the electrolyte. It is necessary to obtain direct confirmation of the structure of the composite film by transmission electron microscopy, which is limited by the lack of methods for removing such films from the substrate.

7. Conclusions

1. The effect of the concentration of polyvinyl alcohol of 17-99 type (low degree of polymerization) in the synthesis electrolyte on the adhesion, electrochemical and electrochromic properties of the cathodically obtained composite nickel hydroxide film was investigated. It is shown that at a concentration of 30 g/l, the film exfoliates and has weak electrochemical and electrochromic properties. The presence of two cathodic peaks (E=500−510 mV and E=560 mV) on the cyclic voltammogram indicates the presence of nickel hydroxide in the PVA matrix and nickel hydroxide with adsorbed PVA. This indicates the dual role of PVA as a surfactant and as a template. At low concentrations, the role of PVA as a surfactant predominates. Increasing the concentration improves the characteristics of the film by enhancing the role of PVA as a template: at 50 g/l, the film does not exfoliate and has good electrochemical and electrochromic characteristics.

2. The effect of polymerization degree of polyvinyl alcohol (17-99, 24-99, and 30-99 types) at a concentration of 40 g/l in the electrolyte on the adhesion, electrochemical and electrochromic properties of the cathodically obtained composite nickel hydroxide film was investigated. It is shown that at a low degree of polymerization, PVA (17-99 type) preferentially plays the role of a surfactant, but is also a template. The film cracks and has mediocre characteristics. The use of medium polymerization PVA (24-99 type) gives a film with high adhesion, electrochemical and electrochromic characteristics. It is shown that in this case, PVA acts as a template; the voltammogram has only one cathodic peak at E=500−510 mV. It was found that the use of PVA with a high degree of polymerization (30-99 type) leads to a significant deterioration in characteristics, including complete peeling of the film. This is probably due to the excess amount of PVA in the film due to the possible secondary adsorption of PVA on the film being formed.

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