

Electrochromic devices are actuation elements of smart windows and allow saving the energy needed to cool the premises. Electrochemical deposition can significantly reduce the cost of electrochromic deposition.

This paper discusses an electrochemical method of deposition based on nickel hydroxide from an electrolyte containing nickel nitrate and polyvinylpyrrolidone (PVP). The electrochromic films were obtained in a galvanostatic mode at different PVP concentrations.

As a result of the studies, it has been shown that the presence of PVP in the deposition electrolyte significantly affects the properties of the resulting electrochromic films. Moreover, the properties of the resulting films strongly depend on the used PVP concentration. Thus, at low concentrations, the addition of PVP causes an improvement in electrochromic and electrochemical characteristics, including stability in the properties of films. While at high concentrations of PVP, the electrochemical and electrochromic characteristics deteriorate significantly up to their almost complete disappearance. The paper proposes a possible mechanism that explains the improvement in the characteristics of the films obtained from the solutions with low PVP concentrations. This mechanism consists in improving the wettability of the substrate, increasing the contact area of the deposit with the substrate and, as a consequence, improving the adhesion and a decrease in the contact resistance at the conductive oxide – Ni(OH)₂ film boundary.

Also, the work has found the range of optimal PVP concentrations for an electrolyte containing 0.1 M Ni(NO₃)₂, which is 0.5–2 %

Keywords: electrochromism, electrochemical deposition, nickel hydroxide, polyvinylpyrrolidone, adsorption, surfactant, nickel nitrate, anode electrochromic material, galvanostatic mode, wettability

A STUDY OF THE INFLUENCE OF POLYVINYL PYRROLIDONE CONCENTRATION IN THE DEPOSITION ELECTROLYTE ON THE PROPERTIES OF ELECTROCHROMIC Ni(OH)₂ FILMS

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1. Introduction

Electrochromic devices are devices that can change their optical characteristics such as the degree of transparency, opacity, reflectivity, and color. One of the options for the application of electrochromic devices can be their use as executive elements of "Smart windows" [1]. At the same time, electrochromic devices can be applied in other areas.

Nevertheless, the greatest prospects for the widespread use of electrochromic coatings as elements of "Smart windows" are in the construction industry [2] since they significantly save the electricity needed to cool buildings. The latter is a powerful argument in the face of the global temperature rise.

It should be noted that the price of electrochromic devices is high [1], and their characteristics are not always stable over time.

Despite the fact that electrochromic devices have not found widespread use yet, the issues of their manufacture as well as the development of new materials are an urgent topic. The proof of their relevance is the dependence of the number of publications containing the keyword "electrochromic device" – Fig. 1. In this case, the given dependence has been growing steadily over the past 30 years. The surge marked in the figure in gray is most likely associated with the 2007–2009 energy crisis.

Electrochromic devices, which can reversibly change their color from transparent to dark, are based on inorganic electrochromic materials. Electrochemical reactions, which occur in the noted materials during current polarization, lead to the appearance of new, intensely colored substances. Examples of such electrochromic materials can be thin films WO₃, NiO, Ni(OH)₂, Ir(OH)₂, etc.

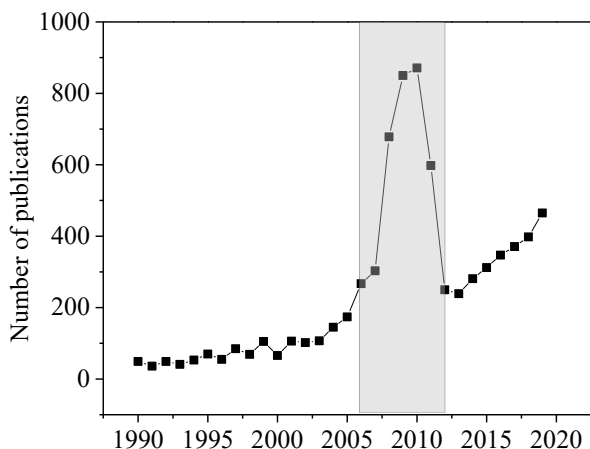


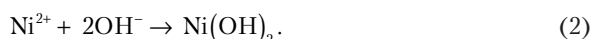
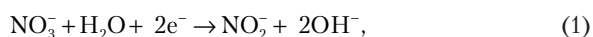
Fig. 1. Number of publications containing the keyword "electrochromic device" according to the "Scopus" database as of 22.07.2020

At the same time, the high price, averaging 500 US \$/m² [1], limits their use. It is determined by several reasons. One of the main reasons is the high cost of vacuum deposition methods, which, on the one hand, give a high-quality homogeneous coating. However, on the other hand, the cost of a spraying unit, maintaining a high vacuum and the energy required for coating, is quite high. Thus, one of the priority tasks of researchers working in this direction should be the development of new, cheaper methods or reduction in the cost of the deposition of the existing ones.

Ni(OH)₂ films are an anodic electrochromic material and can be easily applied electrochemically. This method is cheap, simple, easy to manage, and automate. This paper is devoted to the study and improvement of this deposition method with the addition of a soluble polymer to the deposition electrolyte.

2. Literature review and problem statement

The cathodic template method for obtaining thin, high-quality Ni(OH)₂ films was proposed in [3, 4]. Later, it was modified in the works [5, 6]. The essence of the method is that nickel hydroxide is produced electrochemically by cathodic polarization in a solution containing nickel nitrate and polyvinyl alcohol (PVA). The first component serves as a source of nickel ions as well as nitrate, which enter into electrochemical and chemical reactions, forming a Ni(OH)₂ film in accordance with reactions (1) and (2):



In this case, PVA forms a matrix in an aqueous solution, which is included during deposition into a precipitate. As a result, not a pure Ni(OH)₂ precipitate is formed but a film containing this water-soluble polymer, which is shown in [3]. The composite material Ni(OH)₂-PVA has high adhesion to the substrate and uniformity of coloring during operation. Such a coating can also be dried and stored in a dry state, unlike films obtained without polyvinyl alcohol.

It should be noted that in addition to polyvinyl alcohol, there are other water-soluble polymers, such as polyethylene glycols, polyacrylamides, polyvinylpyrrolidones, etc. [7, 8].

Each of these polymers can be used as a component of electrodeposition solutions to potentially improve the operational properties of the resulting electrochromic films.

One of the widespread water-soluble polymers used in the synthesis of a wide range of inorganic substances is polyvinylpyrrolidone (PVP). On the one hand, this polymer promotes the production of nanostructured materials and acts as a dispersant and surfactant during synthesis. On the other hand, PVP does not significantly increase the cost of synthesis, since it is cheap and produced on an industrial scale for the pharmaceutical industry.

For example, the synthesis of high-quality silver nanowires with high yield without the use of PVP is not possible [9, 10]. This type of material is considered as an alternative to the transparent conductive oxide-based coatings (ITO, FTO, AZO), which are widely used in device displays.

Another example of using PVP is in the work [11]. The researchers synthesized Sb₂S₃ hydrothermal nanowires there for a self-controlled photodetector.

Among other water-soluble polymers, it was also proposed to use PVP as a surfactant in the homogeneous synthesis of BiVO₄. At the same time, Raman spectroscopy showed that, upon addition of PVP, BiVO₄ crystals had the shortest V–O bond length, which led to a decrease in the bandgap to 2.17 eV [12].

A group of researchers studied the deposition of mixed oxides CaO–Al₂O₃–Y₂O₃ and MgO–Al₂O₃–Y₂O₃ from salt–water-soluble polymer xerogels (PVP, polyvinyl alcohol, carbomethylcellulose) [13]. It was shown that, when dried using microwave radiation, the highest oxidation stability in xerogels was observed for those samples that included PVP.

In another study [14], gold nanoparticles were synthesized in the presence of PVP and cetrimonium chloride. In this case, organic components were used to stabilize the resulting nanoparticles.

In turn, using the reaction between PVP and potassium ferrocyanide, the researchers obtained nanoparticles of α-Fe₂O₃ in the form of snowflakes for a photocatalyst [15].

A variant of the synthesis of ultrafine photoactive WO₃ nanoparticles from sols containing different amounts of PVP was shown in [16]. In this case, an increase in PVP led to a decrease in the photoreductive properties, which the authors attributed to an increase in the size of WO₃ nanoparticles.

As can be seen from the above examples, the role of PVP in synthesis is rather broad: from a stabilizer to a reaction component. There are some examples of PVP applications in the synthesis of photochromic and electrochromic coatings below.

The researchers in [17] showed the synthesis of electrochromic films of vanadium oxide. The films were obtained using sol-gel and centrifugation methods. It was shown that during the synthesis, the optimal concentration of PVP was equal to 10 % in the series of 0.5, 10 and 15 %.

The synthesis of Prussian blue by the hydrothermal method in the presence of PVP was shown in [18]. The researchers noted that PVP stabilized dispersion and prevented particle aggregation.

The synthesis of an electrochromic Li₄Ti₅O₁₂ film was implemented by the sol-gel method in [19]. In this case, PVP was used as a sol stabilizer and a substance that prevented cracks in the coating.

The work [20] was devoted to the synthesis of electrochromic films of nickel oxide with the addition of various organic substances. The preparation was carried out electrochemically from a solution containing 0.5 M NiSO₄.

PVP, propylene glycol or sodium lauryl sulfate were added to the deposition electrolyte in an amount of 0.5 wt %. The films were formed in a potentiostatic mode at a working electrode potential of 1 V (CSE). The work noted a strong influence of the presence of the listed substances during deposition, which was expressed in the change of the structural, morphological, electrochemical and electrochromic properties.

However, in this study, only one concentration of PVP was used, and the deposition was carried out in a potentiodynamic mode. Such a mode is characterized by changes in current density over time, which leads to an inhomogeneous structure/ heterogeneity of structure/of the deposit in thickness.

3. The aim and objectives of the study

The aim of this study is to determine the effect of the PVP concentration in the deposition electrolyte containing Ni(OH)₃ during galvanostatic deposition on the electrochemical and electrochromic properties of the resulting Ni(OH)₂ films.

To achieve the aim, the following objectives were set:

- to deposit Ni(OH)₂ films from a solution containing the same concentration of Ni(OH)₃ and different amounts of PVP;
- to determine the electrochemical and electrochromic properties of the obtained films;
- to carry out a comparative analysis of electrochemical and electrochromic characteristics for Ni(OH)₂ films obtained at different concentrations of PVP during deposition.

4. Materials and methods used to determine the effect of PVP addition on the properties of Ni(OH)₂ films

Reagents of analytical frequency were used to prepare solutions in the experiments. All solutions were prepared in distilled water. The experiments used pharmaceutical PVP with a molecular weight of 12,600±2,700.

All films were deposited from solutions under the same conditions. The change concerned only the amount of dissolved PVP, which in deposition solutions was 0, 0.5, 1, 2, 3, 4 wt %. In addition to PVP, the solution contained nickel nitrate (0.1 M). The samples were named in accordance with the amount of PVP: PVP-0, PVP-0.5, PVP-1, PVP-2, PVP-3, PVP-4.

Before coating, the glass coated with a conductive layer of fluorine-doped tin oxide (FTO glass R<10 Ω/sq., Zhuhai Kaivo Optoelectronic Technology Co. Ltd., China) was degreased by wiping with a paste of Na₂CO₃ moistened with water. Next, the substrate was rinsed with running and distilled water, and also sonicated in 96 % C₂H₅OH for 10 minutes (60 W, 41,500 Hz). After that, it was dried and immediately before coating, it was wiped again with a lint-free cloth with ethyl alcohol. In this case, the dimensions of the working zone of the substrate were 2 by 2 cm, the total dimensions were 3 by 2 cm. Then, a Ni(OH)₂ film was deposited with cathodic current polarization [21, 22]. The current density during deposition was 0.1 mA/cm², the deposition time was 10 minutes [23]. The resulting films were dried at room temperature for 1 hour.

Electrochemical and electrochromic measurements.

The electrochemical and electrochromic characteristics of the films were evaluated by the method of cyclic voltammetry (CVA). In this case, changes in the transparency of the samples were recorded in parallel with cycling. The

measurements were carried out according to the three-electrode scheme in the potential window [+201; +701 mV] 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. Nickel foil was used as an auxiliary electrode. A 0.1 M KOH solution served as the electrolyte. The cell was made of transparent polymethyl methacrylate. The diagram of the setup used for the experiments is shown in Fig. 2.

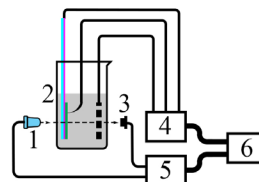


Fig. 2. Simplified diagram of the setup for studying the electrochemical and optical characteristics of electrochromic films: 1 – light source (5,500 K); 2 – cell with free electrolyte and tested electrochromic electrode; 3 – photoresistance; 4 – electronic potentiostat (Elins P-8); 5 – ADC (E-154) and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

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

The potentiostat recorded data at a constant speed of 3 Hz, which was sufficient for integrating the curves by the trapezium method in Microsoft Excel. Integration of the current density (mA/cm²) over time for the cathodic and anodic current densities gave the corresponding specific values of the electricity amount that went into the processes (*Q*, mA·h/cm²).

In turn, the shading depth (*D*, %) was determined from the curves of the transparency change as the difference between 100 % and the transparency (*T*, %) at the moment of maximum darkness (minimum transparency).

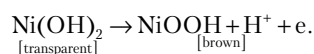
5. Comparison of the obtained characteristics for the film electrodes

5.1. Electrochemical characteristics of the electrodes

The films were obtained for each of the solutions containing different amounts of PVP. Each film was studied by the CVA method, and the data obtained are shown in Fig. 3.

The analysis of the curves' shape allowed us to say that the films obtained from the solutions with different PVP concentrations, to one degree or another, had electrochemical activity. Thus, the anodic peaks on the CVA at about 700 mV corresponded to the oxidation of the Ni(OH)₂ film formed electrochemically – reactions (3), (4).

In the solid phase:



Overall reaction:



At the same time, the cathodic peaks in the range of 550–600 mV corresponded to the reverse processes of NiOOH reduction in Ni(OH)₂.

In this case, the rise in the current in the anodic region corresponded to the release of oxygen and is a side undesirable process – reaction (4):



Note that the CVA of the PVP-0 sample had an additional cathodic peak in the region of 530 mV, which gradually disappeared during cycling. The nature of this peak could be explained by the fact that in the absence of PVP several phases were formed during the deposition in the Ni(OH)₂ film, one of which was metastable and became more stable during cycling. It should be added here that several modifications are known for nickel hydroxide: α -Ni(OH)₂, β -Ni(OH)₂ and an intermediate one between them [26].

A comparison of the CVA curves allowed us to say that the presence of PVP significantly affected the electrochemical characteristics. It should be noted that the film obtained without additives (Fig. 3, *a*) showed a rapid deterioration in electrochemical activity, i. e. the current density peaks decreased from cycle to cycle and practically disappeared by cycle 5. The addition of 0.5 % PVP to the deposition electrolyte dramatically improved the electrochemical characteristics – Fig. 3, *b*. The current peaks did not differ in height from cycle to cycle and practically did not change their position. The CVA for the PVP-1 film was the best in the series in terms of the stability of the curve shape – there were practically no shifts in the position and height of the peaks. A further increase in the PVP concentration led to a gradual decrease in the heights of the cathodic and anodic current density peaks.

In this case, the highest concentration of PVP led to a significant change in the shape of the curve – the appearance of additional peaks and an increase in the current used for the oxygen evolution – Fig. 3, *e*.

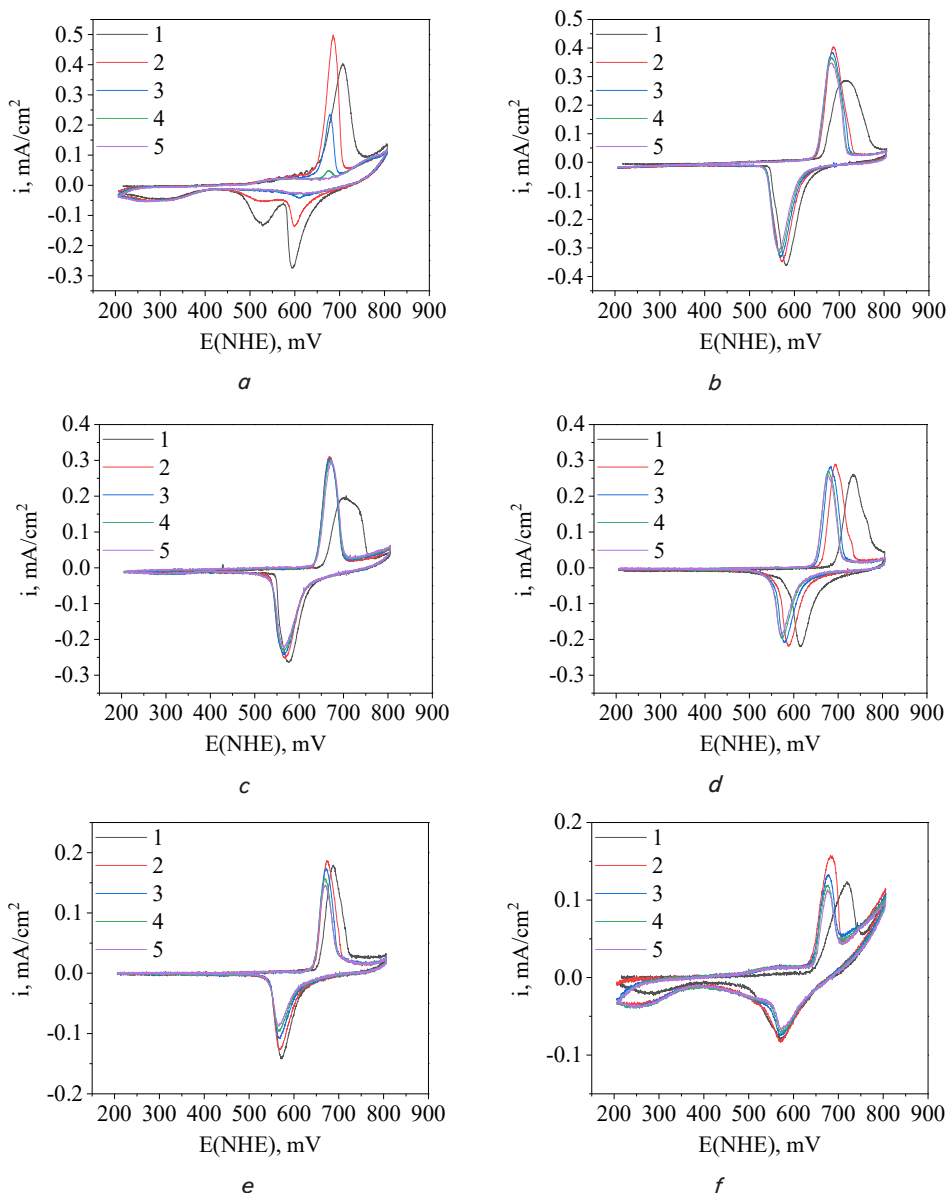


Fig. 3. Cyclic voltammograms for the samples: *a* – PVP-0, *b* – PVP-0.5, *c* – PVP-1, *d* – PVP-2, *e* – PVP-3, *f* – PVP-4

For additional analysis of the curves shown in Fig. 3, the dependence of the total polarization $\eta\Sigma$ on the PVP concentration in the deposition solution was plotted – Fig. 4. The total polarization was calculated as the arithmetic mean of the difference between the cathodic and anodic peaks for each cycle on the CVA.

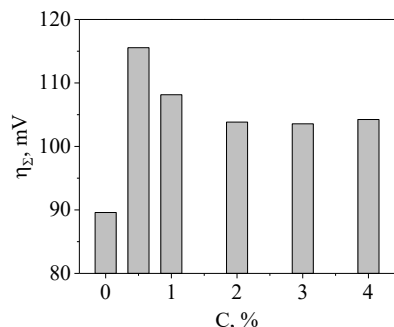


Fig. 4. Dependence of the total polarization on the PVP concentration in the deposition electrolyte

The analysis of the dependence shown in Fig. 4 showed that the film obtained without additives had the lowest total polarization. With the addition of 0.5% PVP, the polarization increased significantly, and with a further increase in concentration, the polarization slightly decreased and remained practically at a constant level. It should be noted that with an increase in the PVP concentration, the polarization did not drop to the value that was in the film obtained without PVP.

The integration of the CVA curves over time can provide additional useful information – specific values of the amounts of electricity used for the corresponding processes. Fig. 5 shows the result of calculating the specific values of the electricity amount in the cathodic and anodic regions/areas of the CVA curves for cycle 5.

The presented graph is interesting in that there is a clear relationship between the concentration of PVP in the solution

and the Q values. When the concentration of PVP grew from 0 to 0.5%, the capacity slightly increased, and then decreased almost linearly. The only exception was the result for the film obtained at the maximum PVP concentration in the series – 4%. At the same time, the curve looked atypical – it contained additional peaks and a large amount of oxygen was released. The latter can be seen from the steep rise in the curve in the potential region above 730 mV. Intensive oxygen evolution can significantly increase the total value of the amount of electricity for anodic processes. This could be the reason for the sharp increase in Q for the PVP-4 sample. An increase in the value for the cathodic process Q can be associated with the reduction of oxygen adsorbed on the electrode, which was released earlier.

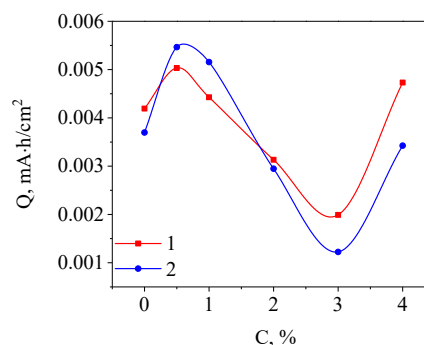


Fig. 5. Dependence of the specific values of the electricity amount of the processes in the cycle 5 of cyclic volt-ampere curves on the concentration of PVP in the deposition electrolyte: 1 – anodic; 2 – cathodic

5. 2. Electrochromic characteristics of the electrodes

The most important thing from the point of view of the consumer are the electrochromic properties of the films. Fig. 6 shows the results of changes in transparency (T , %) during potentiodynamic cycling for each of the obtained films.

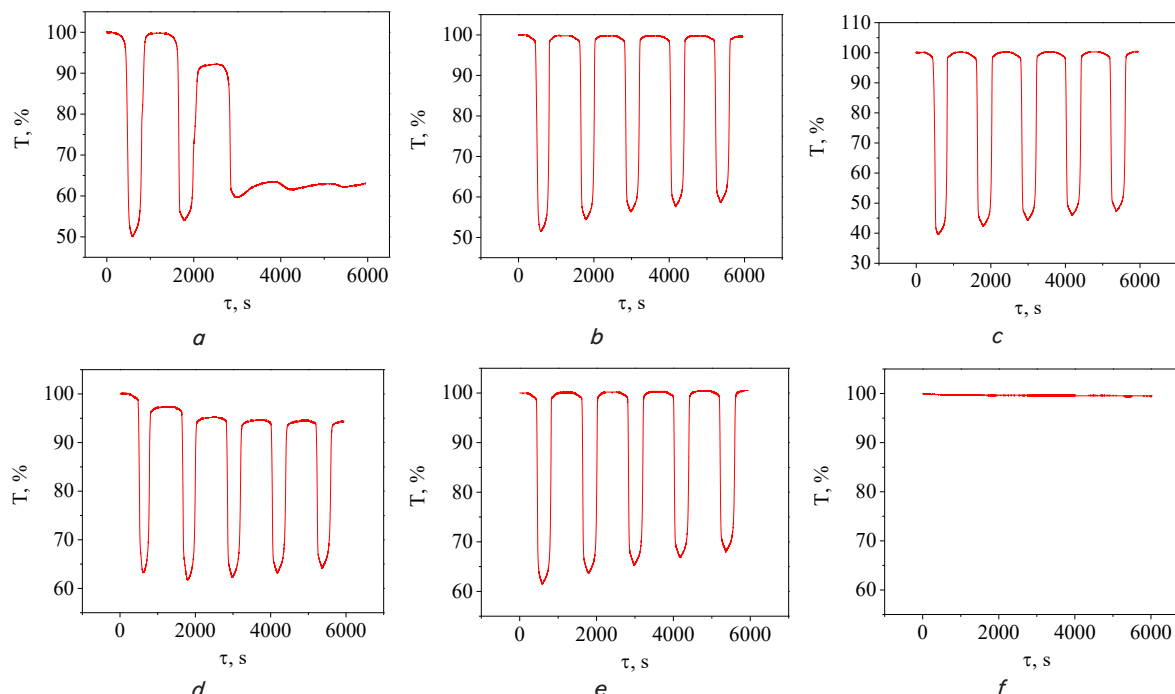


Fig. 6. Curves of changes in transparency over time: a – PVP-0, b – PVP-0.5, c – PVP-1, d – PVP-2, e – PVP-3, f – PVP-4

The curve for the film obtained without PVP (Fig. 6, *a*) illustrated the rapid loss of electrochromic properties since changes in transparency disappeared almost completely by cycle 5. In turn, the addition of 0.5 % PVP led to a significant increase in electrochromic properties – the darkening and lightening processes occurred at all five film cycles. An increase in the PVP concentration to 1 % led to an even greater improvement in characteristics since the shading depth (the difference in transparency in the completely clarified and completely darkened states of the film *D*, %) increased.

With a further increase in the PVP concentration in the electrodeposition solution, the darkening depth decreased and in the case of 4 % PVP, it was equal to about 1 %.

To summarize the data obtained, the average shading depth was plotted depending on the concentration of added polyvinylpyrrolidone in the electrolyte, from which the electrochromic coatings were deposited – Fig. 7.

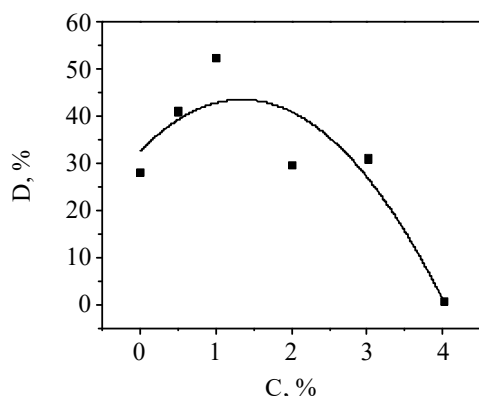


Fig. 7. Dependence of the darkening depth (*D*, %) on the PVP concentration in the deposition electrolyte

As can be seen from the analysis of the graph, the curve has an optimum in the region of 0.5–2 % PVP. The trend line drawn from the experimental values suggests an optimal concentration of 1.35 % PVP.

6. Discussion of the obtained characteristics of the thin-film electrodes from the solutions with different PVP concentrations

The first and unambiguous conclusion that can be drawn from the obtained experimental data (Fig. 5, 7) is that the presence of PVP in the deposition electrolyte significantly affects the properties of the resulting electrochromic films. At the same time, the information on the use in the above papers gives grounds to say that polyvinylpyrrolidone can act as a PVP surfactant. In accordance with this, the presence of surfactants can significantly affect the process of formation and growth of the deposit. In this case, it is possible that the

substance is included in the $\text{Ni}(\text{OH})_2$ deposition and/or accumulated on the surface, also affecting the electrochemical and electrochromic properties.

Based on the analysis of the generalized data (Fig. 4, 5, 7), it can be seen that the optimal concentration of PVP lies in the range of 0.5–2 %. It should be noted that the addition of only 0.5 % PVP dramatically improves the characteristics of the deposit, but at the same time increasing the concentration to 4 % negatively affects all characteristics of the film electrode. It is also worth paying attention to the almost linear decrease in the capacitance of the electrodes, both cathodic and anodic, with an increase in the PVP concentration. Considering the above, it can be assumed that increasing the concentration above 4 % is inappropriate. The proposed mechanism of PVP action is that in solutions containing PVP, the electrode is better wetted [24, 25] and, as a result, a film at the micro-level is formed over the entire surface, including hard-to-reach places of the oxide conductive coating. Thus, due to the increase in the contact area between the substrate and the electrochromic film, the holding force on the surface increases.

A linear decrease in the cathodic and anodic capacities of the processes with an increase in the PVP concentration indicates that the composite structure is most likely not formed. Otherwise, with an increase in concentration, at least in a certain interval, first an increase in this parameter would be observed, and then a decrease. This type of characteristics is observed when polyvinyl alcohol is used instead of PVP [3, 5]. However, this assumption needs to be further verified. If the stated mechanism is correct, then the next step in using PVP is its complex use with polyvinyl alcohol.

It should be noted that the only point that does not fit into the dependence in Fig. 5 is the value of the PVP-4 sample. However, it should be taken into account that when integrating the curve, the anodic region includes the current going for the evolution of oxygen, which in this case is much higher, and the curve in the region of positive potentials goes up sharply. On the other hand, the relatively high value of the cathodic capacity of the PVP-4 sample can be associated with unidentified processes. These processes can be observed in the region of more negative potentials on the CVA – a peak at +260 mV as well as a plateau in the region of +500 mV (Fig. 3, *f*). A possible explanation for these processes is the irreversible reduction of adsorbed PVP on the electrode, which appears at a high polymer content.

7. Conclusions

1. It has been found that the addition of PVP with a molecular weight of $12,600 \pm 2,700$ to the solution for the deposition of electrochromic films based on $\text{Ni}(\text{OH})_2$ at low concentrations improves their electrochromic and electrochemical properties.
2. The range of optimal PVP concentrations in the deposition electrolyte is 0.5–2 %.

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