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THE STUDY OF ACTIVATION IMPACT DURING FORMATION AND TESTING OF $\text{Ni}(\text{OH})_2$ ELECTROCHROMIC FILMS IN THE PRESENCE OF Al^{3+} AND WO_4^{2-} IONS

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Представлене дослідження присвячене спробі поліпшення питомих показників електрохромних плівок на основі гідроксиду нікелю. У роботі проведено дослідження оптичних та електрохімічних характеристик плівок, отриманих через співосадження нікелю з алюмінієм і додаткову модифікацію при циклуванні отриманих зразків. Модифікація була реалізована через циклування плівок в розчинах гідроксиду калію, що містять вольфрамат калію в малих кількостях.

У результаті проведення дослідницької роботи була отримана серія плівок, які демонстрували абсолютно різну електрохімічну поведінку і відрізнялися за своїми оптичними характеристиками. Таким чином було з'ясовано, що спосіб отримання і режим циклування значно впливають на питомі характеристики електрохромних плівок.

Показано, що у потенціодинамічному режимі плівка, отримана без добавок і модифікацій, показала найкращі характеристики. З іншого боку, всі модифіковані плівки, співосадижені з алюмінієм, показали високі характеристики в гальваностатичних режимах, порівняно з еталонною електрохромною плівкою. Скоріш за все, це пов'язано з особливостями фізико-хімічних властивостей плівок, одержаних в присутності добавок.

У свою чергу, використання швидкісного режиму затемнення призводило до погіршення електрохромних характеристик, зокрема до незворотності при освітленні. При цьому, незважаючи на відмінність струмів у різних гальваностатичних режимах в 4 рази, глибина затемнення плівок відрізнялася незначно.

Було також показано, що концентрація 0,3 мМ вольфрамату калію у електроліті циклування призводить до значного погіршення електрохромних властивостей зразків

Ключові слова: електрохромізм, гідроксид нікелю, подвійний шаруватий гідроксид, алюміній, вольфрамат, полівініловий спирт, електроосадження, циклування

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1. Introduction

Technological progress leads to the complication and higher number of developed and used systems and devices. In

turn, this leads to increased consumption of energy and raw materials, which affects ecological conditions. One of a few ways for solving the shortage of resources is a shift towards the rational and frugal usage of resources. This can be helped

with the use of “smart” devices, in which combined use of new engineering solutions, small scale computers, sensors and software allows for a significant reduction in power, time and resources needed for operations [1, 2]. An important aspect of “smart” devices is improved comfort and freedom of the user.

“Smart” windows are a type of “smart” devices, which can be used to solve a range of consumer problems. Improvement of visual comfort, creation of private atmosphere, digital billboards and dynamic design of interiors is far from a complete list of possible use cases. “Smart” windows are devices, which can alter their optical characteristics based on external conditions, user settings. Optical characteristics being color, reflectivity, transparency, glossiness.

The active element of “smart” windows can be based on different systems: liquid crystals [3, 4], electrochemically active materials [5, 6], suspended particles [7, 8]. Commercially produced “smart” windows are most commonly based on solid-state materials in which electrochemical reactions occur [9, 10].

2. Literature review and problem statement

Among electrochromic materials, there are organic [11, 12] and inorganic materials [13, 14]. Organic materials include some polymers: polyaniline, polypyrrole, polythiophenes and metal polymers. Organic electrochromes also include viologens and metal phthalocyanines. The most commonly used inorganic electrochromes are oxides and hydroxides of the following metals: Ti, V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Rh, Ta, W, Ir. Prussian blue is also commonly associated with inorganic electrochromes.

Thin films of $\text{Ni}(\text{OH})_2$ are a promising inorganic material due to high specific electrochromic characteristics [15, 16]. Nevertheless, these characteristics can be improved with the formation of layered double hydroxides, composite materials. The improvement stems from the change in the material's structure and properties on the microlevel.

Methods for improving the characteristics of different electrochromic films are similar and described by several works discussed below.

For instance, the authors of [17] describe the synthesis of a composite $\text{CuWO}_4/\text{WO}_3$ film with improved electrochromic characteristics. The film was prepared using the sparking method. The prepared films had significant porosity, which is characteristic of this synthesis method. The work describes that the prepared film had a significantly higher coloration efficiency of $74.4 \text{ cm}^2/\text{C}$. The obtained value proved to be significantly higher than that of pristine film, which is $49.6 \text{ cm}^2/\text{c}$. Coloration time also decreased from 1.9 s to 1.6 s.

Another work [18] proposes layer-by-layer assembly of tungsten oxide films, containing indium-tin oxide nanoparticles. Such films demonstrated a high switching rate between the colored and bleached states.

Spray pyrolysis method was used to prepare MoO_3 films doped with tungsten [19]. Tungsten-doped films demonstrated better coloration efficiency at W content of 3 %, and at 1 % optimal reversibility was achieved.

A typical method for activating nickel hydroxide films is the deposition of Ni-Me double hydroxide, where Me – Zn, Ti, Fe, Co, Mn, and most commonly Al. Double hydroxides possess improved specific characteristics. A few of the following works describe the synthesis and effect of such modification on electrochromic properties.

The pyrolytic method was used to synthesize aluminum-doped NiO [20]. The authors describe that different aluminum contents lead to different electrochemical characteristics. They found that at the ratio of Ni:Al=19:1, layered double hydroxide (LDH) demonstrated the best characteristics: high transparency (96 %) and wide modulation range (58.4 %). At such ratio of elements in the crystal lattice, high coloration and bleaching rates (1.8 and 4.2 s, respectively) and cycling durability (up to 3000 coloration-bleaching cycles) were achieved.

The papers [21, 22] described that electrochemical and electrochromic properties of Ni-Al LDH can be significantly improved by introducing additives to the cycling electrolyte. For instance, the addition of $[\text{Co}(\text{bpy})_3]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Ru}(\text{CN})_6]^{4-}$, $[\text{Mo}(\text{CN})_8]^{4-}$, $[\text{IrCl}_6]^{2-}$ to the cycling solution or preliminary sorption onto LDH leads to significant improvement in film characteristics. In the paper [23], the same authors report that the introduction of ion mixtures $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Co}(\text{bpy})_3]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$, or $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Ru}(\text{CN})_6]^{4-}$ to the cycling electrolyte also results in a moderate/significant improvement of the characteristics of Ni-Al hydroxide films.

It is also described that the improvement in coloration depth is achieved for the film deposited using cathodic template synthesis when small amounts of aluminum ions are introduced to the deposition electrolyte [24]. The authors also noted the formation of Ni-Al LDH and provide a theoretical basis in favor of adding small amounts of aluminum ions to the deposition electrolyte. The same research group also proposed the addition of small amounts of tungstate ions to the cycling electrolyte [25]. They discovered that the addition of these ions leads to significant improvement in the bleaching rate.

Despite a significant number of works on the preparation of new types of electrochromic materials, the cost and some characteristics of electrochromic devices remain at the current level. Namely, switching time, according to the data of some manufacturers, does not exceed 10 minutes, and the cost reaches $1,000 \text{ USD}/\text{m}^2$ [27]. This is due to the fact that the proposed methods for forming electrochromic films have a high cost for a number of reasons. The main ones: the use of expensive reagents, high power consumption, difficulty of automation. Thus, the development of simple and cheap methods for the deposition of electrochromic films is an important problem.

Based on the information provided in [24, 25], it can be assumed that in case of using tungstate ions in the cycling solution for films containing aluminum, further improvement of electrochromic properties can be achieved.

3. The aim and objectives of the study

The aim of the research is to validate the assumption on the synergetic effect of co-deposited aluminum and cycling of doped films in a solution containing tungstate ions on their electrochromic and electrochemical properties.

To achieve this set aim, the following objectives were set:

- using the cathodic template method, to deposit films with different aluminum contents;
- to cycle the prepared films in solutions with different concentrations of tungstate ions;
- to conduct a comparison of the obtained data for determining the possible synergetic effect.

4. Materials and methods used for the preparation and study of electrochromic device

Film deposition. The film was deposited in a single compartment cell with nickel foil counter-electrode. Glass slide coated with fluorine-doped tin oxide was used as a substrate (FTO glass, Zhuhai Kaivo Optoelectronic Technology Co., China). The sheet resistance of FTO glass $\approx 9 \Omega/\square$. The working area of the substrate was 2×2 cm. Before the deposition, the substrate was thoroughly washed with distilled water. It was the wash in ethanol to remove any remaining residue. Deposition conditions and compositions of cycling electrolytes, along with sample labels are listed in Table 1.

Characterization of the electrochromic device. Electrochemical tests were conducted using the digital potentiostat connected to a PC (Elins, P-8, Russia) in potentiodynamic and galvanostatic regimes, using the three-electrode setup.

Conditions and sample labels

No.	Label	Deposition conditions	Deposition electrolyte	Cycling electrolyte
1	Reference	Cathode 0.1 mA/cm ² , 30 °C, 10 min	50 g/L PVA *, 0.01 M Ni(NO ₃) ₂	0.1 KOH
2	1Al-1W		50 g/L PVA, 0.01 M Ni(NO ₃) ₂ , 0.138 mM Al(NO ₃) ₃	0.1 M KOH, 0.1 mM K ₂ WO ₄
3	1Al-3W		50 g/L PVA, 0.01 M Ni(NO ₃) ₂ , 0.138 mM Al(NO ₃) ₃	0.1 KOH, 0.3 mM K ₂ WO ₄
4	2Al-1W		50 g/L PVA, 0.01 M Ni(NO ₃) ₂ , 0.275 mM Al(NO ₃) ₃	0.1 M KOH, 0.1 mM K ₂ WO ₄
5	2Al-3W		50 g/L PVA, 0.01 M Ni(NO ₃) ₂ , 0.275 mM Al(NO ₃) ₃	0.1 KOH, 0.3 mM K ₂ WO ₄

Note: PVA – polyvinyl alcohol

Cycling was conducted in a cell with free electrolyte volume. Nickel foil was used as a counter-electrode and Ag/AgCl(KCl sat.) as a reference electrode. Optical characteristics were recorded in parallel to electrochemical tests, using the setup shown in Fig. 1.

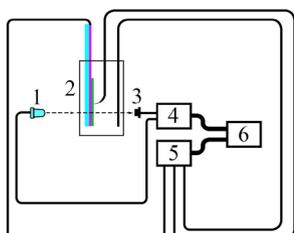


Fig. 1. Simplified schematic of the setup for characterization of electrochromic films: 1 – light source (5500 K); 2 – cell with free electrolyte and studied electrochromic electrode; 3 – photoresistor; 4 – ADC; 5 – digital potentiostat; 6 – computer

The setup includes the E-154 analog-to-digital converter (Russia) and software supplied along with it.

Each electrochromic electrode was cycled in different regimes which are listed in Table 2.

Table 2

Cycling regimes used in sample characterization

Regime	Parameters
Potentiodynamic regime (PD)	$E_1=+201$ mV, $E_2=+751$ mV; $v=1$ mV/s
Galvanostatic regime No. 1* (GC1)	$I_a=+0.96$ mA; $\tau_a=33.6$ s; $I_k=-0.96$ mA; $\tau_c=33.6$ s
Galvanostatic regime No. 2** (GC2)	$I_a=+1.92$ mA; $\tau_a=16.8$ s; $I_k=-1.92$ mA; $\tau_c=16.8$ s
Galvanostatic regime No. 3*** (GC3)	$I_a=+0.48$ mA; $\tau_a=67.2$ s; $I_k=-0.48$ mA; $\tau_c=67.2$ s

Note: for galvanostatic regimes No. 1, 2 and 3, the currents were chosen as the peak current of (I_{cp}) of the 5-th cycle of the reference sample (no additives): * – $I_{(charge)}=-I_{cp}$; $I_{(charge)}=+I_{cp}$; ** – $I_{(charge)}=-2I_{cp}$; $I_{(discharge)}=+2I_{cp}$; *** – $I_{(charge)}=-0.5I_{kn}$; $I_{(discharge)}=+0.5I_{cp}$.

At the end of each potentiodynamic cycling, the films were photographed for visual evaluation of film quality.

Table 1

5. Analysis and comparison of characteristics of prepared films

To compare the effect of aluminum and/or tungstate ions in the cycling electrolyte, the reference film was deposited without any additives, which was cycled in the potassium hydroxide electrolyte without additives. The recorded characteristics are shown in Fig. 2.

The analysis of the obtained results reveals that the film darkens well, while the coloration degree (the difference between transparency (T) in the colored and bleaching state) is rather high and on average is equal to 86 % (Fig. 2, b). It can also be seen that there is some degradation of electrochromic properties during cycling, irreversibility I increases. The value I is the difference between 100 % and film transparency in the bleached state on the last cycle. At the same time, cyclic voltammogram (CV) has asymmetric peaks of oxidation and reduction processes (Fig. 2, b). Additionally, the degree of film development is observed, as the cathodic peak current density increases with each new cycle. Photographs of the film in the colored state demonstrate that the film is uniform and has saturated coloration.

The film with minimum aluminum content cycled in the solution with minimum potassium tungstate content demonstrated significantly different characteristics (Fig. 3). The CV curve of this sample has more symmetric peaks, with the cathodic peak on the first cycle having the value of 0.4 mA/cm². In general, the shape of the curve indicates that the electrode reaction is more reversible. However, the coloration degree of the 1Al-1W sample is lower, with the value of about 73 %, with irreversibility being almost 0 % (Fig. 3, b). The film has uniform coloration and doesn't have any visible defects (Fig. 3, c).

The results for the film containing aluminum and cycled in a solution with high potassium tungstate content (1Al-3W sample) are shown in Fig. 4.

This sample shows significant changes in the CV curve in comparison to previous samples, which can be described as a gradual decrease of cathodic peak currents along with the appearance of a plateau (Fig. 4, a). The coloration-bleaching curve shows a decrease in the coloration degree. The averaged D value is 63 %. The irreversibility is almost non-existent. It should be noted that film coloration is non-uniform (Fig. 4, c).

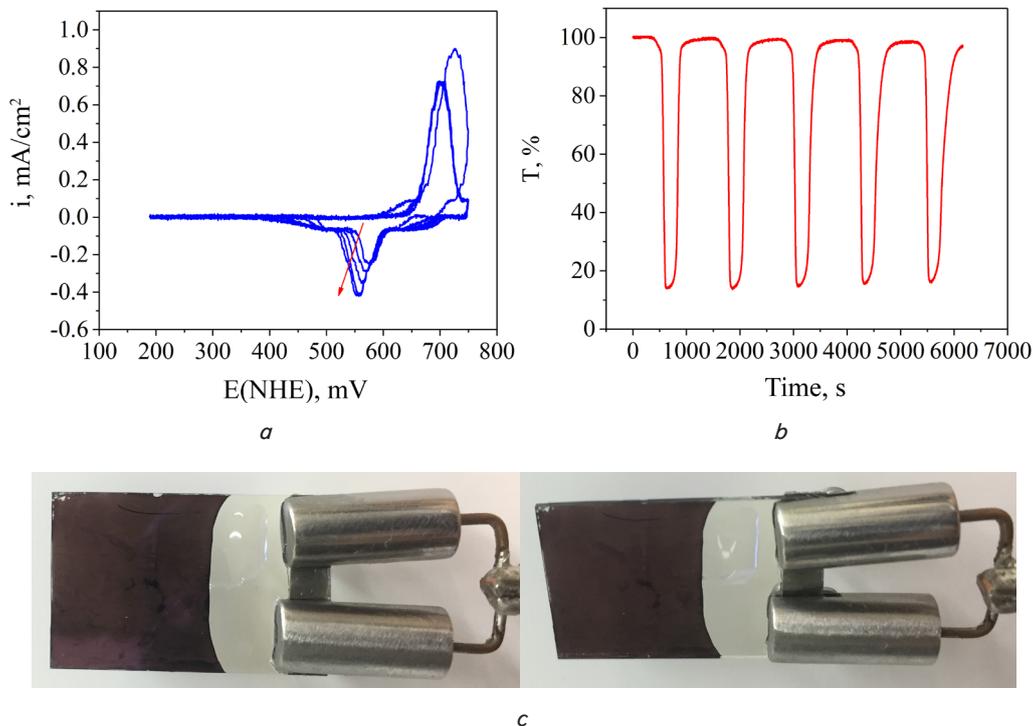


Fig. 2. Potentiodynamic cycling results for the reference sample of potentiodynamic cycling: *a, b* – CV curve (arrows highlight changes during cycling) and coloration-bleaching curve; *c* – photographs of the electrode in the colored state

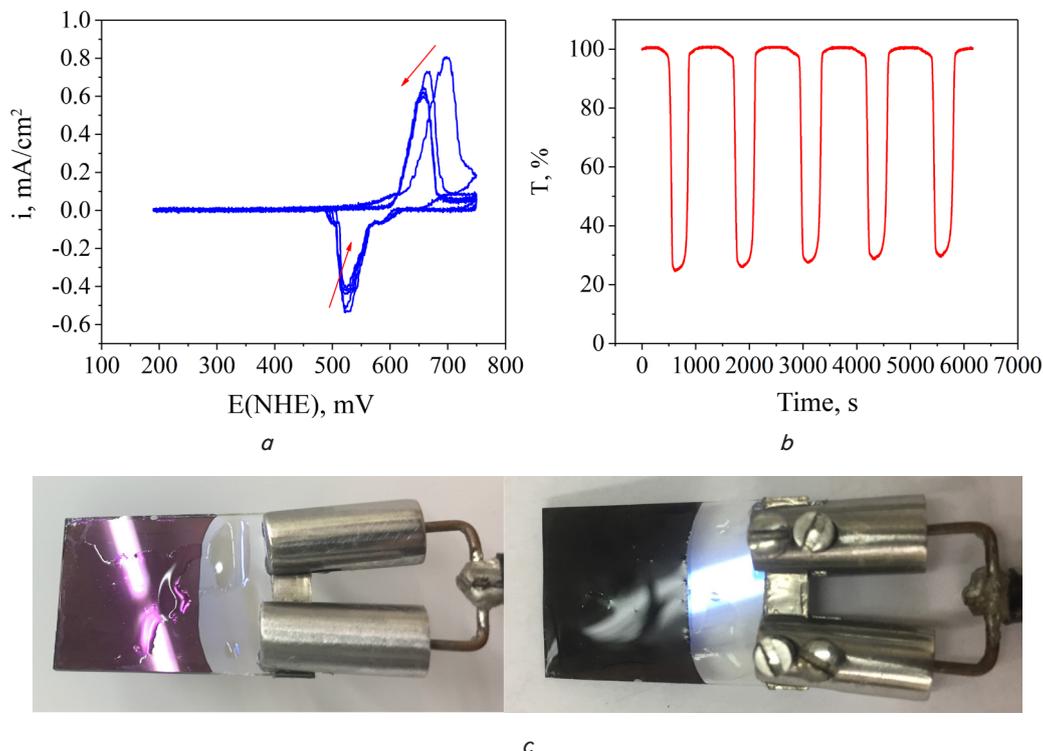


Fig. 3. Potentiodynamic cycling results for the 1Al-1W sample: *a, b* – CV curve (arrows highlight changes during cycling) and coloration-bleaching curve; *c* – photographs of the electrode in the colored state

Fig. 5 shows the results obtained for the 2Al-1W film. In case of higher aluminum content and cycling in the electrolyte with minimum potassium tungstate content, the film is similar to the previous 1Al-3W film. The CV curve also shows the broadening of the cathodic peak and

decrease of the anodic peak. The coloration-bleaching curve is similar to the previous sample, however, the value *D* is somewhat lower – 56 %. Film coloration is rather patchy, which can be seen on the photograph of the film after cycling (Fig. 5, *c*).

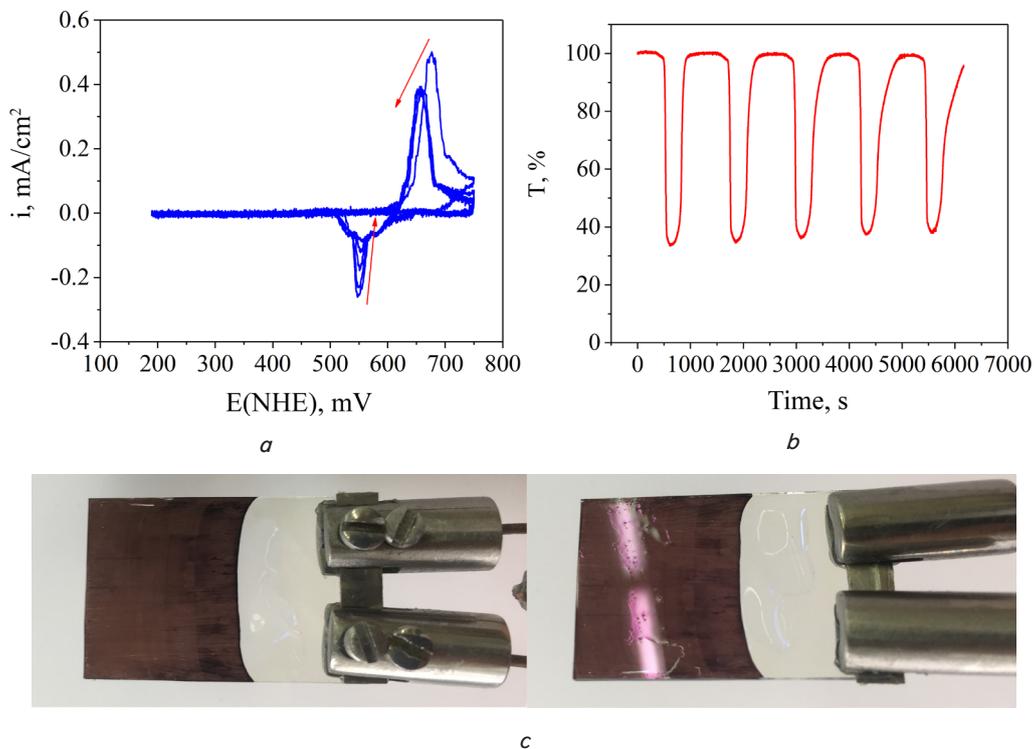


Fig. 4. Potentiodynamic cycling results for the 1Al-3W sample: *a, b* – CV curve (arrows highlight changes during cycling) and coloration-bleaching curve; *c* – photographs of the electrode in the colored state

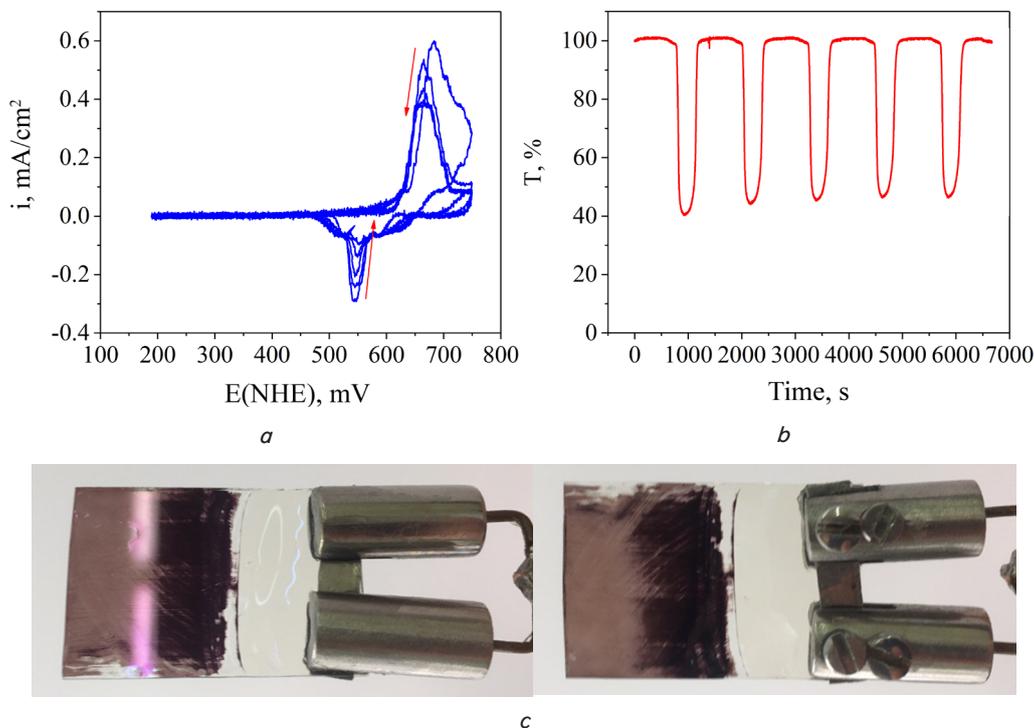


Fig. 5. Potentiodynamic cycling results for the 2Al-1W sample: *a, b* – CV curve (arrows highlight changes during cycling) and coloration-bleaching curve; *c* – photographs of the electrode in the colored state

The characteristics of the last film, prepared with a maximum content of additives to deposition and cycling electrolytes (2Al-3W film) are shown in Fig. 6.

This doesn't show the broadening of the cathodic peak, but a decrease of current density is observed. The anodic current density remains almost constant through-

out the cycling of this sample (Fig. 6, *a*). The coloration degree is somewhat lower than that of the previous film ($D=64\%$), and no irreversibility of the bleaching process is observed. The photograph of the film reveals patchy coloration, while color saturation is high (Fig. 6, *c*).

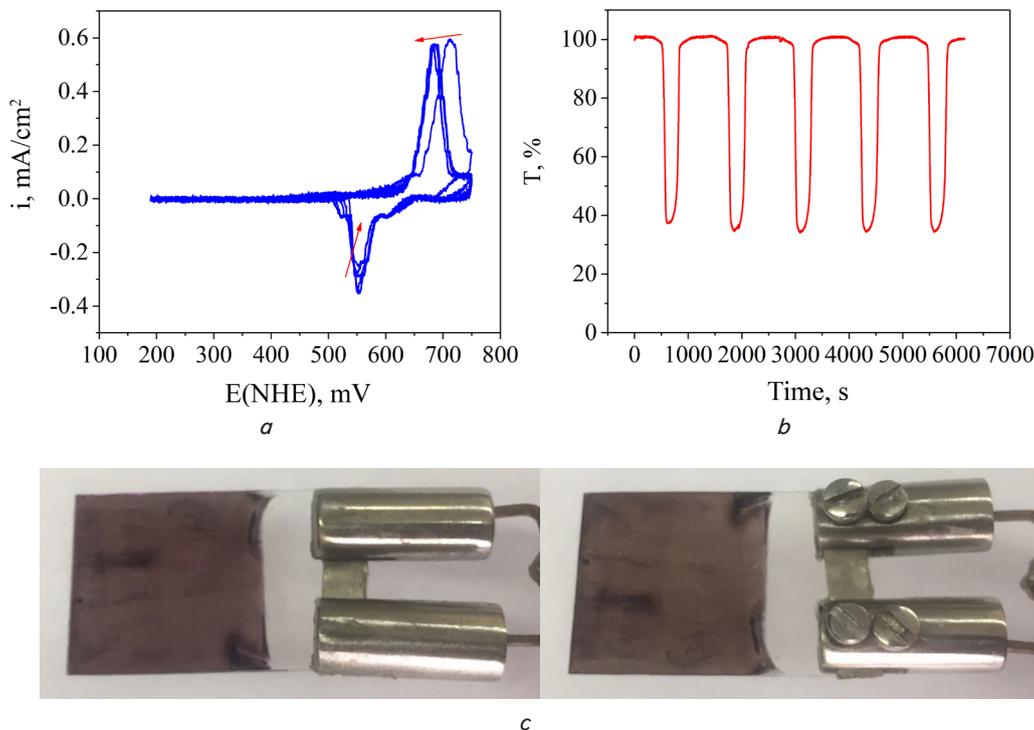


Fig. 6. Potentiodynamic cycling results for the 2Al-3W sample: *a*, *b* – CV curve (arrows highlight changes during cycling) and coloration-bleaching curve; *c* – photographs of the electrode in the colored state

Histograms were plotted for all films: dependency of average coloration degrees and irreversibility on cycling regime (Fig. 7, 8).

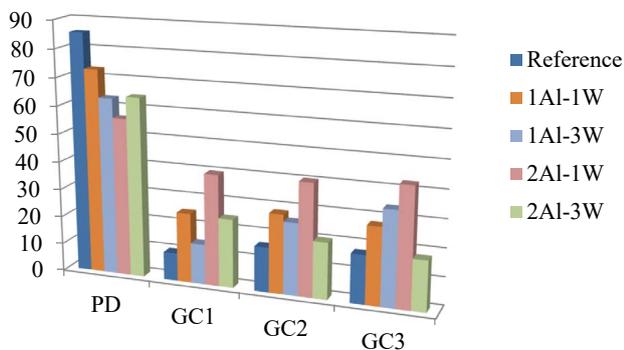


Fig. 7. Coloration degree (*D*) for the samples used in the study depending on regime

It should be noted that the coloration-bleaching curves for galvanostatic regimes (GC1–3) were omitted to avoid clutter. Nevertheless, the obtained values (*D*, *I*) were plotted for comparison of variable electrolyte compositions and cycling regimes. Despite high specific characteristics of the reference films in the potentiodynamic (PD) regime, it performed the worst in other regimes (Fig. 7). It is also interesting that all the films with additives had a high coloration degree with the 2Al-1W sample being optimum for galvanostatic regimes. Further increase in tungstate concentration results in a lower coloration degree in potentiodynamic and galvanostatic regimes. Irreversibility values (*I*) for different films and regimes are shown in Fig. 8.

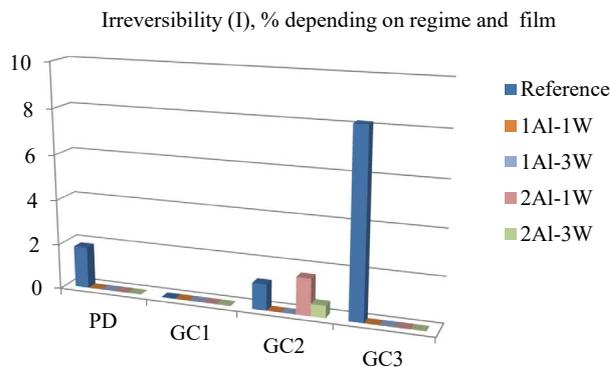


Fig. 8. Irreversibility (*I*) of the samples used in the study depending on regime

The analysis of the presented dependency shows that higher irreversibility is demonstrated by the reference film. Additionally, the high-rate regime (GC2) has a negative impact on the reversibility of the films.

6. Discussion of data obtained for electrochromic device

The analysis of the histograms shown in Fig. 7, 8 allows outlining a few interesting patterns. Thus, the analysis of the averaged coloration degree values for different films and regimes allows concluding that:

1. The use of potentiodynamic regimes (CV) allows for deeper film coloration in comparison to other regimes.
2. Small amounts of aluminum in the deposition solution, possibly, lead to the improvement of specific characteristics,

as the reference film and 1Al-1W have similar values of coloration degree. The shape and peak current density values indicate better reversibility of the 1Al-1W sample. Nevertheless, due to the codeposition of aluminum resulting in the film having less electrochemically active nickel to partake in the reaction, the results of both films are almost identical. This conclusion is true, at least in the context of coloration degree. Determination of nuances requires a detailed study of the concentration range from 0 to 0.275 mM Al³⁺.

3. It is interesting that the films, which demonstrated average results during potentiodynamic cycling, showed better results during galvanostatic cycling. It was obvious that the films activated with both aluminum and potassium tungstate had low average coloration degree values (D) among all films during potentiodynamic cycling. However, these films show significantly higher values in galvanostatic regimes (GC1, GC2 and GC3) in comparison to the reference sample. The only exception is the film with the highest amount of additives – 2Al-3W. It is also interesting that despite regimes GC1, GC2 and GC3 having current ratios of 1 to 2 and to 0.5, this didn't have much effect on the coloration degree of the films.

The obtained data can be interpreted as follows. Both aluminum and tungstate activate electrochromic nickel hydroxide films, they differ in their action. It would seem that for aluminum as an activator, a broader study is required to find the optimal concentration. The combined effect of both activators does manifest, but the process might be slow and the effect is seen after prolonged cycling, which also calls for additional studies. It is obvious that exceeding some limit concentration values, as in case with both aluminum and tungstate leads to a decrease in film properties.

The analysis of the second histogram is less interesting, however, some major tendencies can be outlined:

1. The highest irreversibility value is observed for the films cycled in the GC2 regime.

2. The highest irreversibility value is demonstrated by the reference sample and samples activated with 0.138 mM Al(NO₃)₃ and 0.3 mM K₂WO₄.

The No. 1 conclusion for the second dependency is related to the following. It is assumed that the non-activated films have a lower proton diffusion coefficient and/or smaller specific surface area, and stop working properly in the high-rate regime. The reason for this may be the physico-chemical features of Ni-Al double hydroxide, which are most likely formed under such conditions. Thus, it becomes obvious that real devices favor "soft" slow regimes and partial coloration for longer cycle life.

In summary, the following conclusion can be made. The use of aluminum during deposition along with cycling in the presence of tungstate ions shows some activating effect, which is manifested in galvanostatic regimes. Thus, the combined use of both activation types (during deposition and cycling) does manifest and is supported by the analysis of experimental results.

Further development can be the search for optimal concentrations of ions used in this study. The use of other ions can also be considered.

7. Conclusions

1. It was found that the addition of 0.138 to 0.275 mM Al(NO₃)₃ and 0.1 to 0.3 mM K₂WO₄ to the deposition and cycling solution, respectively, results in a decrease of coloration degree to ≈30 % in the potentiodynamic regime, but to an increase in galvanostatic regime to ≈25 % in comparison to the reference sample.

2. The addition of 0.3mM K₂WO₄ to the cycling solution along with the codeposition of aluminum (0.275 mM) results in a significant decrease in the properties of electrochromic films, which manifests in all regimes – coloration degree decreased by up to ≈25 %.

3. Three films demonstrated irreversibility from 0.5 to 1.6 % in the GC2 regime, which is due to this regime having high cycling current. So, it is suggested to use "soft" slow cycling regimes and partial coloration for real devices for long cycle life.

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