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EFFECT OF VARIABLE TEMPERATURE LOADS ON CHARACTERISTICS OF ELECTROCHROME COMPOSITE $Ni(OH)_2$-PVA FILMS

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Electrochromic coating is the basis of smart windows with variable optical characteristics. Nevertheless, despite the obvious advantages of using smart windows in construction, their cost is high.

We have considered the coatings obtained by the cathodic template method, which are more economical in production. The presented studies are devoted to tests at cyclic temperature loads – repeated cooling and heating. The paper shows the influence of the medium and the method of heat supply (removal) to an electrochromic electrode based on a composite $Ni(OH)_2$-PVA coating as well as the effect of surface preparation before its application.

As a medium for cyclic temperature loads, we used air or a working electrolyte – 0.1 M KOH. As a preliminary preparation of the transparent electrically conductive base, we used electrochemical etching of a part of the layer of the electrically conductive transparent coating of tin oxide doped with fluorine in a solution of 1 M HCl.

The result of a series of experiments was the discovery of a strong influence of temperature cyclic loads on the final characteristics of electrochromic films. The electrochromic film on the sample, which was subjected to cyclic temperature changes in air and on the substrate without etching, almost completely lost its electrochromic characteristics and adhesion. The sample, which was subjected to thermal stress in an alkali solution, lost its uniformity during coloring.

On the other hand, both films, which were deposited on etched substrates, had generally better characteristics than samples deposited without etching and subjected to thermal stress in the air and in alkali. In this case, the sample, which was obtained on the substrate with pretreatment by etching and subjected to temperature cycling in alkali, had even slightly better characteristics than the reference sample

Keywords: electrochromic device, electrochemical deposition, nickel hydroxide, template, polyvinyl alcohol, temperature tests, adhesion

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1. Introduction

Electrochromism, a phenomenon associated with a change in the color of a substance under the influence of an electric current, has been known for a long time [1]. However, systems that use in practice the phenomenon of electrochromism for a controlled change in the color characteristics of various elements have appeared relatively recently. So, for example, only one of the latest lines of American aircraft Boeing 787 Dreamliner contains electrochromic windows, which can be dimmed or brightened in a controlled manner, including at the request of the passenger [2]. At the same time, the widespread use of such systems in construction as components of smart windows is limited, primarily due to their high price.

For industrial production, primarily oxide multilayer systems with lithium-based electrolytes are used [3]. Moreover, each layer performs its own functional role.

Electrochromic layers change their color due to an electrochemical reaction. Depending on the process during which the color change occurs, electrochromic materials are classified as either anodic or cathodic [4]. Nickel oxides and hydroxides are one of the promising anodic electrochromic materials [5].

In the industry, the application of electrochromic materials, including nickel oxides, is carried out by vacuum deposition methods, which significantly increases the cost of the final product [6]. However, there are many other options for applying electrochromic materials. Electrochemical deposition methods are the most promising ones [7], since they are cheap to implement, easily automated, and make it possible to control the properties of the resulting electrochromic coatings in a wide range.

It should be noted that, provided the price of smart windows with electrochromic devices is significantly reduced, the benefits from their use will be substantial. The literature sources have shown that smart windows can save up to 49 % of the electricity required for air conditioning [8]. Also, when using them, the load on the power grids decreases during the peak periods of consumption.

So, the study and improvement of electrochemical methods of electrochromic materials deposition are an important task on the way to reduce the cost of electrochromic devices.

2. Literature review and problem statement

In [7], the possibility to obtain high-quality electrochromic composite films of $Ni(OH)_2$-polyvinyl alcohol (PVA) by the electrochemical method was shown. Also, the main parameters of production on nickel substrates as an element of smart mirrors were clarified.

The use of a transparent substrate of fluorine-doped tin oxide deposited on glass (FTO glass) for the deposition of $Ni(OH)_2$-PVA films was described in [9]. In a series of experiments, it was shown that the optimal concentration of PVA for the deposition of high-quality electrochromic films in the electrolyte was 4 %. In addition, the study revealed a number of important relationships – viscosity, electrical conductivity, and density of solutions containing PVA and nickel nitrate.

In turn, on the basis of mathematical modeling of the processes in [10], the optimal parameters for obtaining $Ni(OH)_2$ films by cathodic deposition were clarified, namely: current density and reagent concentration. Moreover, in the same work, the key influence of the resistance of an electrically conductive substrate on the uniformity of deposited films in thickness was shown.

It was shown that preliminary shallow etching of an electrically conductive base helped to obtain electrochemically more uniform $Ni(OH)_2$-PVA films with high electrochemical and electrochromic properties [11]. This etching was called soft and led to the formation of a developed surface and an increase in the surface wettability of the electrically conductive transparent coating on the glass.

It should be noted that electrochromic devices must operate at different temperatures and may be subject to temperature extremes during operation. Considering that the composite electrochromic film has a different temperature coefficient of expansion as compared to the substrate, peeling of the film from the substrate is possible with temperature drops. Such peeling can result in degradation of the performance of the electrochromic device.

In [12], it was shown that exposure at extremely high temperatures in an electrolyte (8 hours in 0.1 KOH at 80 °C) led to a significant deterioration of the electrochromic properties of films based on $Ni(OH)_2$ and PVA. Nevertheless, the authors attributed this deterioration to the recrystallization of $Ni(OH)_2$ into a less active form, since exposure to the same conditions in air, on the contrary, somewhat increased the electrochemical and electrochromic characteristics of the deposit. Thus, the researchers in their experiments were limited only to exposure for a long time.

Several works are worth noting in which the effect of thermal gradients on various films, coatings, and device elements was investigated.

For example, in [13], the adhesion of water-based acrylate coatings to the frames of wooden windows was investigated. The researchers concluded that temperature cycling had little effect on coating adhesion.

In the paper devoted to the adhesion of nickel coatings deposited from solutions without the use of electricity on a polypropylene substrate, the effect of temperature cycling was shown [14]. The number of temperature cycles was 9, 12, 15, and 18, while the cycling occurred in the range from –25 to +27 °C. As a result of the study, it was shown that after temperature cycling, the adhesion of the metal coating to the polymer did not change.

The work [15] described the study of a ceramic thermal barrier coating based on zirconium and yttrium oxides with additives. A series of tests demonstrated that the adhesion strength of the topcoat changed significantly after thermal cycling and isothermal soaking. It was also found that thermal fatigue damage depended on the thermal cycling option.

The authors in [16] considered the improvement of the method for evaluating thermal barrier coatings using a laser. The study showed that short pulses of laser radiation were more damaging than long pulses.

One of the main reasons that explained the decrease in adhesion between dissimilar layers was the different temperature coefficient of expansion of materials [17]. The latter led to the appearance of stresses when the temperature changed. At the same time, the authors of this paper studied the interaction of a substrate made of organic material and an anisotropic conductive film in contact with an integrated microcircuit. One of the conclusions was that delamination was more dependent on the material of the anisotropic conductive film.

In [18], a study was made of the adhesion of the sealant to the glass of a photovoltaic module. In this case, a combined effect was carried out on the compound by means of different temperature and humidity of the environment. It was shown that the greatest degradation of adhesion occurred near the open border.

[19] also studied the effect of accelerated thermal cycling on the integrity of the semiconductor-metal layer in a commercial photovoltaic solar cell. It was shown that the bond at the Si-Ag interface was stronger than that at Al-Si. At the same time, cracks easily appeared and grew during thermal cycling in the range of –40 °C to 90 °C.

Analysis of information from literary sources gives grounds to say that testing multilayer coatings and devices after thermal cycling is one of the primary tasks. Taking into account the fact that for the electrochromic $Ni(OH)_2$-PVA coating no tests were carried out for the effect of thermal gradients, this stage was implemented in this study.

3. The aim and objectives of the study

The aim of the study is to determine the effect of variable temperatures on the electrochemical and electrochromic properties of composite $Ni(OH)_2$-PVA films. Moreover, the characteristics to be determined are valuable information for improving the electrochemical method of deposition and implementation of electrochromic devices based on this electrochromic coating.

As part of solving this aim, the following objectives have been formulated:

– to determine the effect of variable temperature loads on electrochromic $Ni(OH)_2$-PVA films on FTO glass substrates in air;

– to determine the effect of variable temperature loads on electrochromic $Ni(OH)_2$-PVA films on FTO glass substrates in 0.1 M KOH;

– to evaluate the morphology of the obtained films and compare their quality after thermal tests.

4. Research methods used to determine the thermal gradients effect on the properties of $Ni(OH)_2$-PVA films

All films were obtained on glass with an electrically conductive transparent coating consisting of tin oxide doped with fluorine, then FTO glass – R<10 Ohm/sq., Zhuhai Kaivo Optoelectronic Technology Co. Ltd. (China).

Fig. 1 shows a simplified scheme of experiments to clarify the features of obtaining electrochromic films in the study.

Before applying composite coatings or before carrying out the procedure of soft etching, the FTO glass was degreased by wiping with a paste based on water and soda. Next, the substrate was rinsed with running and distilled water, and also treated with ultrasound in an ultrasonic bath in 96 % ethyl alcohol (10 minutes, 60 W, 41.5 kHz). After that, they were dried, and before the next operation wiped again with a lint-free cloth with ethyl alcohol. In this case, the dimensions of the working area of the FTO glass were 2×2 cm, the total dimensions were 3×2 cm.

As mentioned earlier, soft etching not only improves the quality of the deposited films [11] but also creates a relief surface. A substrate with a developed surface can significantly change the properties of the electrochromic coating deposited on it. In this series of experiments, soft etching was performed in the gentlest mode at very low currents so as not to significantly change the value of the surface electrical conductivity of the substrates. The etching mode was chosen as follows –0.25 mA, 10 s; +0.25 mA, 100 s; –0.25, mA 40 s; +0.25 mA, 100 s; –0.25, mA 40 s; +0.25 mA, 100 s. 1 M HCl was used as a solution for soft etching. After etching, the substrates were thoroughly rinsed in distilled water, and an electrochromic coating was applied.

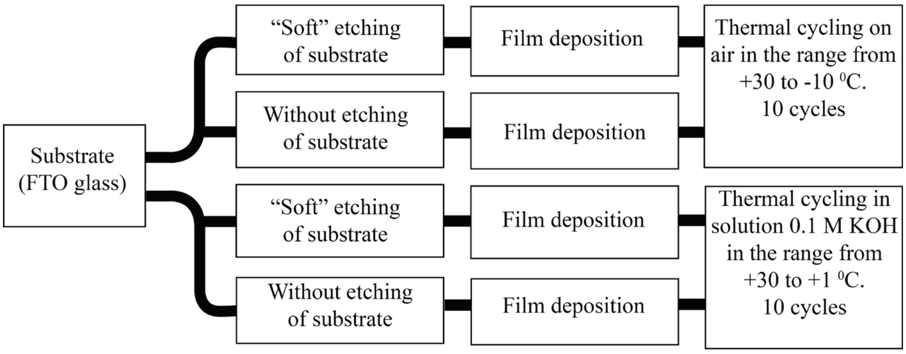


Fig. 1. General scheme of experiments to study the thermal gradients effect on the properties of composite $Ni(OH)_2$-PVA films

The electrochromic coatings were obtained electrochemically using cathodic template deposition from a 0.01 M $Ni(NO_3)_2$ solution with 4 % PVA at i=0.1 mA/cm^2 for 600 s. The deposition mode was the same for all samples. In addition to the four types of films obtained (Fig. 1), an additional film on FTO glass was obtained, which was not subjected to temperature cycling. This film was used as a reference for comparison with others. All films were dried at room temperature for 1 hour. After that, the films were subjected to temperature cycling in the modes shown in Fig. 1. It should be noted that in order to increase the rate of the temperature change of the samples in air, the glasses with coatings were attached to an aluminum radiator with a large area (Fig. 2). In this case, the uncoated side was facing the radiator surface, and the temperature range was expanded in the negative direction since the water-based solution did not allow this. The use of an aluminum radiator and expansion of the temperature range were done to increase the thermal stress in the samples.

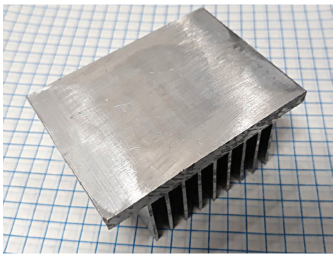


Fig. 2. Aluminum radiator for thermal cycling in air

In all cases, the temperature was recorded using a UNI-T UT70B digital multimeter (China) and a standard thermocouple included in the kit.

After temperature cycling, all films were tested by cyclic voltammetry with the parallel recording of optical characteristics. We also tested the film that was not subjected to temperature cycling. To simplify the description, the samples were designated according to Table 1.

Table 1

Sample designations

Substrate	Without etching	With etching	Without etching	With etching	Without etching
Temperature cycling medium	----------	Air	Air	Alkali solution	Alkali solution
Temperature range, °C	----------	+30÷–10	+30÷–10	+30÷+1	+30÷+1
Designation	Standard	Air-SE	Air	Alkali-SE	Alkali

Electrochemical measurements.

The electrochemical characteristics were assessed by the potentiodynamic cycling method. The measurements were carried out using a three-electrode scheme [18]. Cycling was performed in the [+201; +701 mV] mode relative to the normal hydrogen electrode (NHE) at a sweep rate of 1 mV/s and at 10 mV/s. A silver chloride electrode in a saturated KCl solution was used as a reference electrode. Nickel foil was used as an auxiliary electrode. The electrolyte was a 0.1 M KOH solution. The cell was made of transparent plexiglass. During cycling, along with the electrochemical data, changes in the optical characteristics of the films were also recorded. For the experiments, we used the setup shown in Fig. 3.

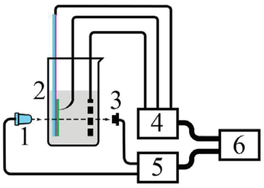


Fig. 3. Simplified diagram of the setup for studying the electrochemical and optical characteristics of electrochromic films: 1 — light source (5,500 K); 2 — cell with free electrolyte and electrochromic electrode under test; 3 — photoresistance; 4 — electronic potentiostat (Elins P-8); 5 — ADC (E-154)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

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.

Morphology and visual evaluation of electrodes.

To compare the quality of the films after temperature and electrochemical cycling, the electrodes were darkened by unrolling the potential of the film electrode from +201 to +701 mV (NHE) at a sweep rate of 10 mV/s. Next, the electrode surface was examined under an optical microscope (Carl Zeiss, Germany), and photographs were taken without magnification.

5. Comparison of the obtained characteristics for film electrodes

5. 1. Characteristics of a film electrode that has not been subjected to variable thermal stresses

Data for the untreated film (the Standard sample) are shown in Fig. 4. Analysis of the cyclic voltammetry curve shows stability in the position and height of the peaks, starting from the third (the directions of changes with cycles are shown by an arrow). The specific current density for the oxidation process of $Ni(OH)_2$ in NiOOH approximately equals 0.6 mA/cm^2 and for the reverse (cathodic) process approximately equals 0.5 mA/cm^2. In addition, a small rise at potentials more positive than +700 mV is associated with a small amount of oxygen released from the electrolyte [20, 21]. The coloration-bleaching curve is shown in Fig. 4, *b*. In this case, the ordinate axis (T) is the transparency in %. It should be said that also, starting from the third cycle, the coloration depth (D) stabilizes and practically does not change further. It should be noted that the coloration depth here refers to the difference between (T) in the lightened and darkened states. In this case, for example, for the first cycle (Fig. 4, *b*), D will be equal to 100–78=22 %. Thus, it can be concluded that the film obtained under standard conditions and without treatment works stably.

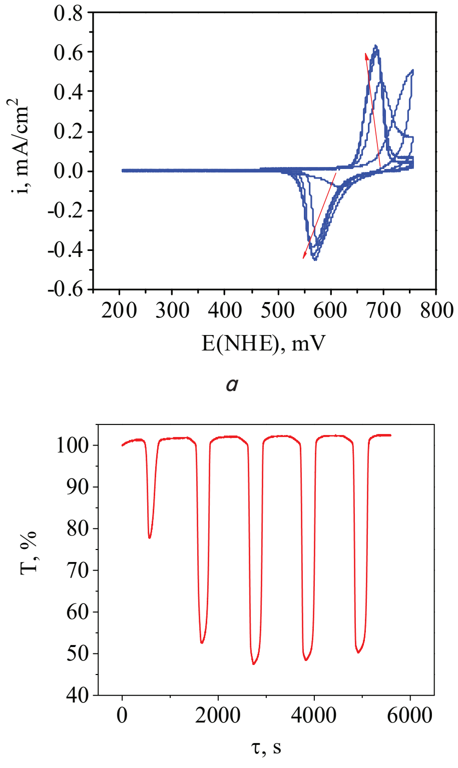
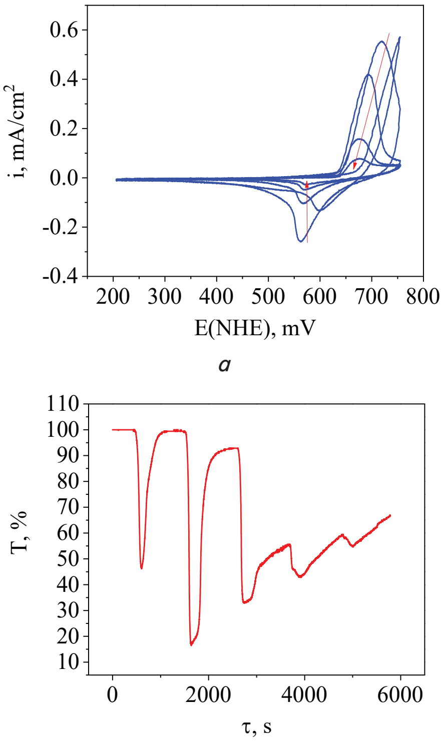


Fig. 4. Characteristics for the Standard sample: *a* — cyclic voltammetry curve (CVA) recorded at a speed of 1 mV/s; *b* — coloration-bleaching curve during potentiodynamic cycling

5. 2. Characteristics of film electrodes subjected to variable thermal stresses in air

The curves for the film obtained on a base without soft etching of an electrically conductive base and treated in the air are shown in Fig. 5. When analyzing the shape and course of the CVA curve, it is seen that the electrochemical characteristics begin to deteriorate from the second cycle. In this case, the specific densities of the peak currents sharply decrease (Fig. 5, *a*) (changes are shown by arrows). The decrease in the values of the peak current densities is more than 10 times. Moreover, a clear deterioration in characteristics is also seen on the coloration-bleaching curve (Fig. 5, *b*). Firstly, the coloration depth decreases, and secondly, the electrode does not return to 100 % transparency during the bleaching process. Thus, by the end of the cycle, the electrode remains in a partially colored state.

Interestingly, in this case, the electrode deposited on the substrate, which was subjected to the procedure of soft etching and temperature cycling in the air (like the previous sample), has characteristics similar to the Standard sample. The specific current densities of the peaks of the cathodic and anodic processes are similar in magnitude for a sample that was not exposed to thermal gradients.

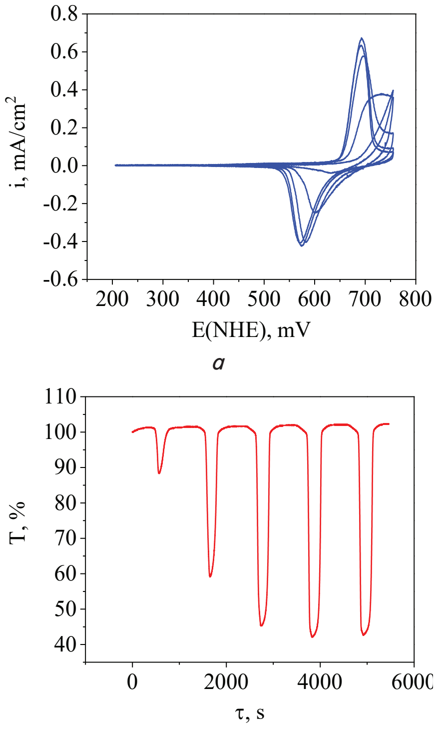


a

b

Fig. 5. Characteristics for the Air sample: *a* – cyclic voltammetry curve (CVA) recorded at a speed of 1 mV/s; *b* – coloration-bleaching curve during potentiodynamic cycling

Moreover, the Air-SE sample has a similar coloration-bleaching curve with the Standard sample (Fig. 4, 6). The coloration depth of the Air-SE sample is even greater than that of the Standard one.



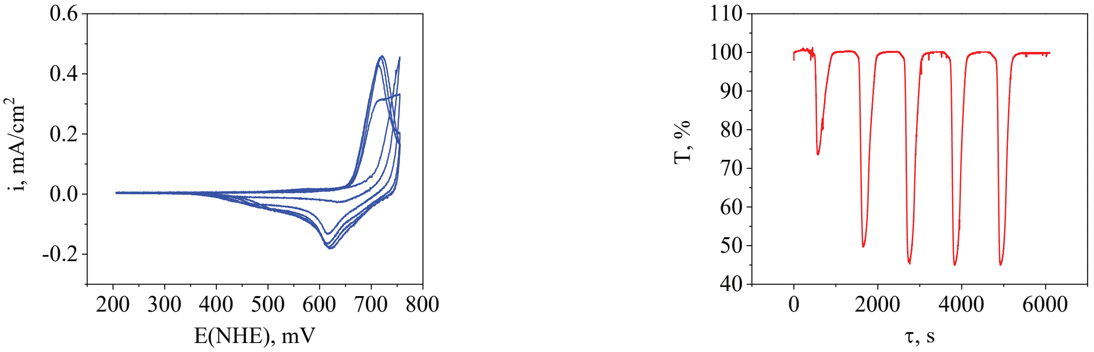
a

b

Fig. 6. Characteristics for the Air-SE sample: *a* – cyclic voltammetry curve (CVA) recorded at a speed of 1 mV/s; *b* – coloration-bleaching curve during potentiodynamic cycling

5. 3. Characteristics of film electrodes subjected to variable thermal tresses in 0.1 M KOH

The CVA and the coloration-bleaching curves obtained for the samples subjected to variable thermal stresses in the working alkaline solution are shown in Fig. 7, 8. It should be immediately noted that, compared to the reference sample, these films have a different form of CVA curves. In this case, the cathode peaks seem to consist of several peaks that form a plateau. It is also worth noting that the anode peaks have shifted towards more positive potentials compared to the Standard sample. In this case, the anodic peak for the Standard film is at a potential of +684 mV, while the corresponding peaks for the Alkali and Alkali-SE samples lie in the range from +704 to + 714 mV. In this case, despite the fact that processes leading to a change in the CVA forms occur in the alkali, the coloration-bleaching curves did not change significantly in comparison with the Standard sample (Fig. 4, *b*, 7, 8, *b*).



a

b

Fig. 7. Characteristics for the Alkali sample: *a* – cyclic voltammetry curve (CVA) recorded at a speed of 1 mV/s; *b* – coloration-bleaching curve during potentiodynamic cycling

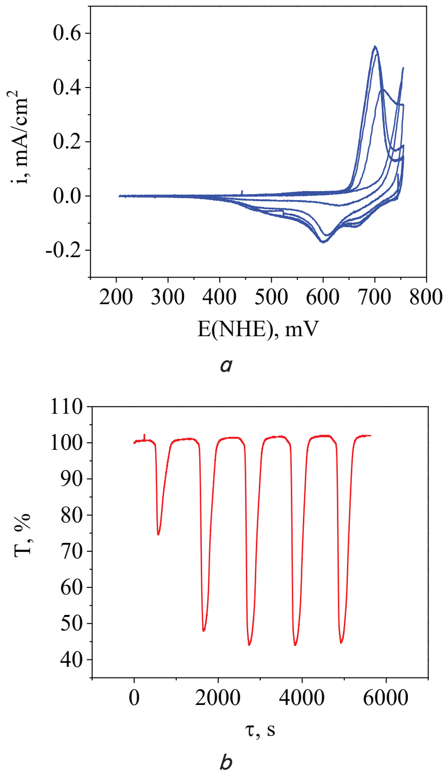


Fig. 8. Characteristics for the Alkali-SE sample: *a* — cyclic voltammetry curve (CVA) recorded at a speed of 1 mV/s; *b* — coloration-bleaching curve during potentiodynamic cycling

5. 4. Comparison of the parameters of film electrodes obtained from CVA and coloration-bleaching curves

In order to quantitatively evaluate the change in the electrochemical characteristics of the films from cycle to cycle, CVAs were processed by the method of numerical integration to obtain the specific capacities of cathodic and anodic processes. The specific capacities of anodic processes depending on the number of the CVA cycle are shown in Fig. 9; specific capacities of cathodic processes are shown in Fig. 10.

An analysis of the presented dependences made it clear that only the sample, the base of which was not subjected to soft etching followed by temperature cycling in the air (the Air sample), had radically different characteristics. The specific capacities of the cathodic and anodic processes were initially higher than those of the other samples (1st and 2nd cycles) but then, they dropped sharply. Taking into account that the Air sample had poor electrochromic characteristics (Fig. 4, *b*), and the coloration depth in the fifth cycle (D_5, Fig. 11) was the lowest, it can be argued that the greatest thermal gradients effect was observed in this sample.

In addition, it can be noted that all samples that were deposited on etched substrates had larger coloration depths than the corresponding samples without etching (Fig. 11).

In conclusion, it should be noted that the coloration depth of all samples that were subjected to temperature cycling was slightly greater than that of the Standart sample.

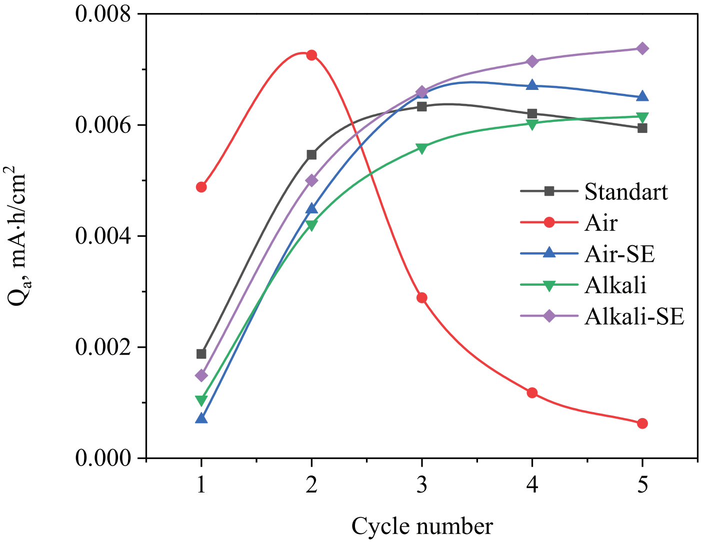


Fig. 9. Specific capacities of anodic processes on CVA obtained in a series of samples

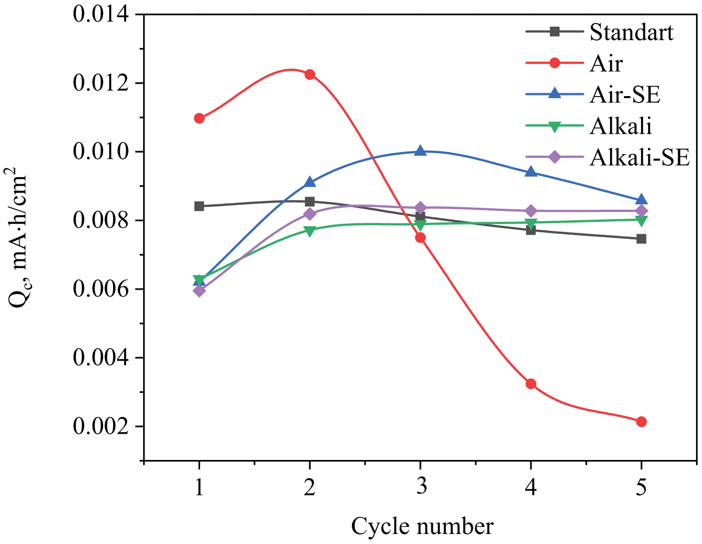


Fig. 10. Specific capacities of cathodic processes on CVA obtained in a series of samples

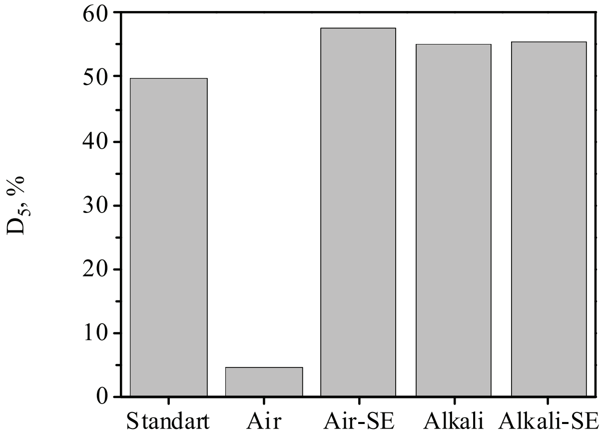


Fig. 11. Coloration depth on the fifth cycle for samples of the series

5. 5. Optical microscopy and qualitative evaluation of the film electrodes used in the study

To evaluate the effect of temperature treatment, the samples were colored and photographs were taken in the colored state without magnification and using an optical microscope (Fig. 12–16).

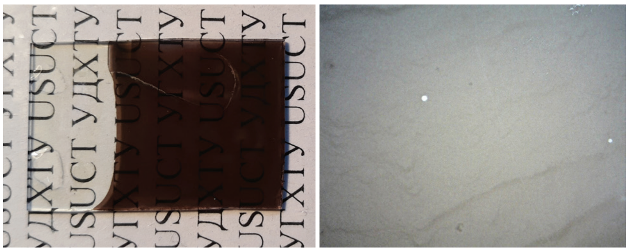

a *b*

Fig. 12. Photographs of the Standard electrode in a colored state: *a* – no magnification; *b* – 80x magnificatio

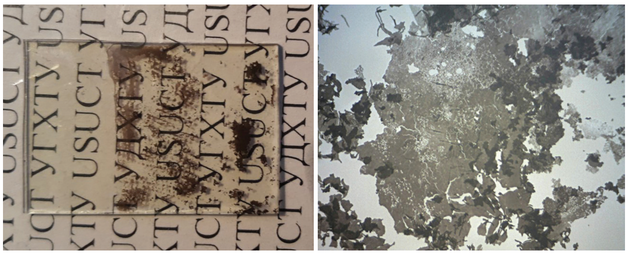

a *b*

Fig. 13. Photographs of the Air electrode in a colored state: *a* – no magnification; *b* – 80x magnification

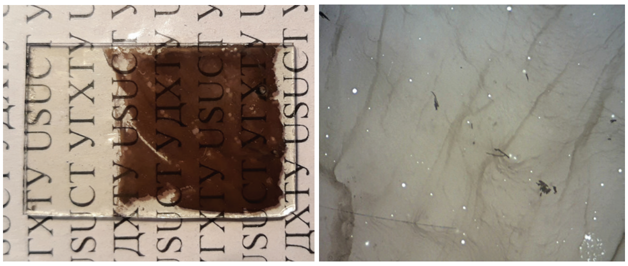

a *b*

Fig. 14. Photographs of the Air-SE electrode in a colored state: *a* – no magnification; *b* – 80x magnification


a *b*

Fig. 15. Photographs of the Alkali electrode in a colored state: *a* – no magnification; *b* – 80x magnification

Analysis and comparison of photographs of the samples shown in Fig. 12–16 led to the following important observations. The best uniformity of the colored coating was for the Standard, Air-SE, and Alkali-SE samples, that is, for the electrode that was not exposed to variable temperatures, and for all electrodes that were deposited on the etched base. On the other hand, in the sample pairs exposed to temperature changes in the air and in the solution, better uniformity was observed for glasses deposited on FTO, the surface of which was partially etched. Moreover, the Alkali-SE sample had the most uniform color among all treated samples. At the same time, the Air sample had the worst state, since even without magnification the photograph showed that the electrochromic coating was practically absent (Fig. 13, *a*). In the photograph with magnification, this sample had cracks in the coating, and even individual layers of the coating were on other layers, and they were clearly visible (Fig. 13, *b*).


a *b*

Fig. 16. Photographs of the Alkali-SE electrode in a colored state: *a* – no magnification; *b* – 80x magnification

So, it is obvious that the process of soft etching is a very important operation from the point of view of the developed technology.

6. Discussion of the characteristics of film electrodes treated at variable temperatures

Obviously, the temperature ranges taken at 29 °C and 40 °C are clearly greater than those to which assembled electrochromic devices can be exposed. Moreover, a sharp drop even from +30 to +1 °C in real conditions is unlikely. However, such a stress test is useful as it provides an estimate of the maximum operating range for electrochemically deposited coatings.

It is also worth noting that multiple drops of 10–15 °C are more than possible since the service life of electrochromic devices is tens of years. At the same time, an increase in the temperature range and a decrease in the time change of these temperatures in model experiments can help to evaluate the effect of long-term heating-cooling cycles.

Evaluation and analysis of the entire data make it possible to evaluate both the heating-cooling of films without contact with the working electrolyte (the Air series) and when the films are in the electrolyte (the Alkali series). In this way, the Alkali series shows the behavior of the electrodes in the assembled device, while the Air series is an indicator of changes, for example, when the components of the electrochromic device are stored in dry warehouses.

The obvious conclusion from all the data is that temperature differences are an important factor that cannot be neglected in the development, design, and implementation of finished devices.

It turned out quite unexpectedly that temperature cycling in the air had a greater effect on films than cycling in the electrolyte since the presence of films containing nickel hydroxide in the electrolyte led to structural changes [22]. These changes were associated with recrystallization and contributed to the deterioration of the characteristics of the films. However, the explanation for this fact may lie in the fact that since the researchers wanted to achieve a temperature difference in the shortest possible time, the films were attached to a large area aluminum radiator. As a result, the temperature drop occurred in a very short time (Fig. 17). Recorded curves for two samples of the Air and Alkali sample series showed that the temperature change was faster in air (Air). At the same time, in about 15 minutes, the temperature dropped by almost 35 °C. Moreover, since the uncoated side was lying on the radiator, there was a large temperature gradient in the Al (radiator)→glass→FTO coating→$Ni(OH)_2$ structure. Considering that the mass of the sample was small, while the mass, area, and thermal conductivity of the radiator were large, a colossal temperature gradient was created between the electrode layers. This, apparently, led to a sharp deterioration in the characteristics of the films, which was reduced to partial delamination of the latter from the electrically conductive substrate. According to observations, during the cycling of the electrode, a part of the film peeled off into the electrolyte. When an attempt was made to rinse off the electrolyte with distilled water, the electrochromic coating was completely removed.

At the same time, the samples that were in solution (the Alkali series) were rinsed by the solution from all sides and did not undergo such a sharp change in temperature. Moreover, the aqueous solution acted as a buffer between the outside temperature and the electrode. In this way, the time required to reduce the temperature from +30 to +1 (i.e. 29 °C) was 37 minutes. Therefore, during treatment in the electrolyte, changes in the characteristics of the film were not so sharp, however, they still took place. Interestingly, after temperature tests in alkali, the shape of the curves changed significantly. Obviously, this is due to the fact that there were changes in the structure associated with the decomposition of α-$Ni(OH)_2$, which was obtained electrochemically and transformed into β-$Ni(OH)_2$ and other phases [23–28].

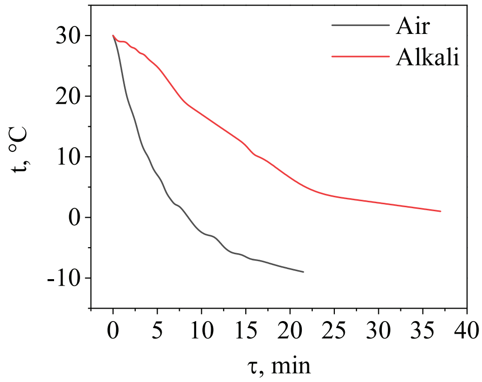


Fig. 17. Curves of temperature changes during cooling for samples of the Air and Alkali series

The most important conclusion can be drawn when comparing samples from the same series. Thus, all samples deposited on a coating partially etched by the soft etching method had better characteristics than when the coating was deposited on a substrate without etching. Moreover, in the Air series and the electrode etched after extreme temperature changes, most of the coating remained on the electrode and darkened well. In the case of the Alkali series, the etched-backed coating was similar in the state and characteristics to the reference sample (the Standard sample).

Obviously, etching, on the one hand, creates better wettability with the solution from which electrochemical deposition takes place. As a result, the coating is deposited in hard-to-reach places. On the other hand, etching increases the microroughness of the electrically conductive transparent coating and the contact area between it and the electrochromic coating [11]. This microroughness is the point at which the coating is held during thermal expansion or contraction. The latter definitely has a positive effect on the characteristics of film electrodes.

To sum up, the process of soft etching of an electrically conductive transparent oxide can be recommended as an obligatory technological operation in factories before coating substrates with electrochromic materials.

7. Conclusions

1. Samples that were subjected to temperature cycling in air and deposited on substrates without treatment lost their electrochromic properties irreversibly. By the 5^{th} cycle, the coloration depth of such films was 4.8 % versus 49.9 % for the untreated film electrode. In this case, the coloration depth of the sample obtained on the etched surface of FTO glass, which was also exposed to temperature changes in the air, was 57.5 %.

2. It is shown that repeated cyclic action of variable temperatures on films in alkali affected to a lesser extent than in air. In this case, by the 5th cycle, the coloration depths for films deposited on FTO glass and etched FTO glass were 55.2 and 55.5 %, respectively. The lesser degree of influence in the solution was associated with uniform heating of the samples from different sides as well as with thermal inertia. The latter led to a smoother change in the sample temperature.

3. Analysis of the morphology and qualitative characteristics of the samples showed that, in the general case, cyclic temperature changes negatively affected the adhesion of the film to the surface. In this case, the loss of adhesion was expressed both in the complete delamination of the film and in the loss of the ability to coloring locally without delamination. At the same time, among the films treated, the sample that was exposed to variable temperatures in the alkaline solution and had an etched substrate had the best quality characteristics.

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