



EFFECT OF DEPOSITION TIME ON PROPERTIES OF ELECTROCHROMIC NICKEL HYDROXIDE FILMS PREPARED BY CATHODIC TEMPLATE SYNTHESIS

Kotok V. A.^{1,3}, Kovalenko V. L.^{2,3}, Solovov V. A.², Kovalenko P. V.⁴, and Ananchenko B. A.⁵

¹The Department of Processes, Apparatus and General Chemical Technology, Ukrainian State University of Chemical Technology, Gagarin Ave, Dnipro, Ukraine

²The Department of Analytical Chemistry and Food Additives and Cosmetics, Ukrainian State University of Chemical Technology, Gagarin Ave, Dnipro, Ukraine

³The Department of Technologies of Inorganic Substances and Electrochemical Manufacturing, Vyatka State University, Moskovskaya str., Kirov, Russia

⁴Vyatka State University, The Institute of Continuing Education of Russian and Foreign Citizens, Moskovskaya str., Kirov, Russia

⁵The Department of Inorganic and Physical Chemistry, Vyatka State University, Moskovskaya str., Kirov, Russia

E-Mail: Valeriy_e-ch@ukr.net

ABSTRACT

Electrochromic films based on nickel hydroxide have been deposited from $\text{Ni}(\text{NO}_3)_2$ solution employing cathodic template synthesis. Polyvinyl alcohol has been used as a template. The influence of deposition time (10, 20, 40 and 80 min) on electrochromic and electrochemical properties of the film had been studied. By means of scanning electron microscopy and atomic force microscopy it was determined that prepared films are uniform, its morphology is independent of substrate morphology, surface bumps are 30-100 nm in diameter and their height is below 180 nm. By mean of X-ray diffraction analysis established that film consists of highly defective $\alpha\text{-Ni}(\text{OH})_2$ with low crystallinity. Electrochemical and electrochromic properties of films prepared at different deposition times have been studied by means of cyclic voltammetry with simultaneous recording of bleaching-coloration curves. Analysis of bleaching-coloration curves has revealed high reversibility of the process. It was also discovered that in series of deposition times 10 - 20 - 40 - 80 min, the average coloration degree was 0.3 - 0.5 - 0.65 - 0.75, which corresponds to 70% - 31% - 17% increase in coloration degree. As such, the optimal deposition time for nickel hydroxide films at a current density of 0.625 mA/cm^2 is 40 - 80 min (film thickness 2.58 - 5.16 μm).

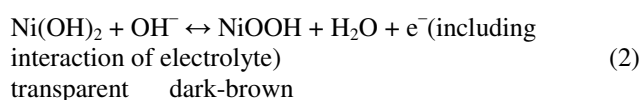
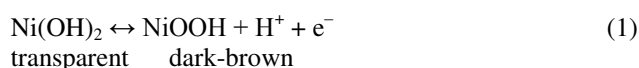
Keywords: template synthesis, electrochromism, nickel hydroxide, smart windows, transparency change, thin films.

INTRODUCTION

Interested towards synthesis methods of nickel hydroxide is caused by its wide range of application, such as electrode material for electrochemical devices, alkaline batteries and supercapacitors [1 - 6], electrocatalyst for oxidation of organic compound for organic synthesis or for use in fuel cells [7 - 10]. In addition, one of the application nickel-based layered double hydroxide is a synthesis of highly stable pigment for cosmetic purposes [11].

In turn, electrochromic devices find their use in glassing of buildings, cars, planes for creating comfortable lighting and saving power for conditioning. Nickel hydroxide thin films can be used in electrochromic windows and electrochromic mirrors. The later can be used in the light tunnel for adjusting light emission, in rear-view mirrors of a car, in order to increase safety during driving, and also as a decorative element for interior design.

Optical state of electrochromic elements can be changed between transparent (reflective) and colored. In electrochromic elements employing nickel hydroxide film a solid-state electrochemical reaction occurs, which can be described by equation (1) or summarized equation (2) [12-18].



Nickel hydroxide belongs to anodic electrochromes because color change occurs upon oxidation. In addition, based on deposition method and following treatment, the nickel hydroxide can have an intermediate composition of $\text{Ni}(\text{OH})_x\text{A}_y \cdot n\text{H}_2\text{O}$ type, where A - acid anion [19]. As a counter-electrode in electrochromic devices, it is reasonable to use cathodic materials based on tungsten oxide. This is because dark-brown color of oxidized $\text{Ni}(\text{OH})_2$ film in combination with the dark-blue color of reduced WO_3 , would result in almost complete black.

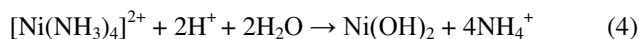
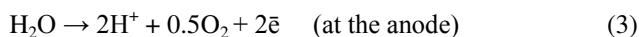
Electrochromic devices employ thin film electrodes and nickel hydroxide film must meet following requirements: high transparency, high adhesion to the substrate, high coloration degree and complete bleaching during cycling and high cycling stability. At the same time, for wide adoption of electrochromic devices, nickel hydroxide deposition methods should be convenient in realization and should allow film deposition on a piece of various sizes and should be easy to automate. As of



present, there are many known methods for nickel hydroxide deposition [20 - 21]: vacuum evaporation, sputtering, spray pyrolysis, sol-gel, electrodeposition etc.

The most convenient for industrial application is an electrochemical method for nickel hydroxide deposition. This is explained by the ease of control and automation of deposition process, which utilizes already known procedures and equipment from galvanic industry. Use of electrical current in combination with other parameters (electrolyte composition, temperature etc.) allows to effectively control deposition process and quality of resulting films.

There are two known electrochemical methods for deposition of $\text{Ni}(\text{OH})_2$ films - anodic deposition and cathodic deposition [22 - 33]. In the first case, the deposition occurs because of acidification of anodic region (reaction 3), which leads to decomposition of nickel ammine complex according to reaction 4. In second case deposition occurs as a result of nitrate ion reduction with the formation of OH^- (reaction 5), which react with Ni^{2+} according to reaction 6:



Anodic deposition is less convenient because ammine complex is unstable and decomposes upon evaporation of ammonia with the formation of nickel hydroxide, which deposits on all surfaces at phase boundary, including equipment. This also results in the evolution of toxic ammonia. As such, this method is not suitable for large-scale production. Cathodic does not have this issue, and such is recommended for industrial application.

Regardless of the deposition method, the main issue of nickel hydroxide film is adhesion to the conductive substrate. In order to improve adhesion, we have proposed cathodic template synthesis with polyvinyl alcohol (PVA) as the template [6, 34 - 37]. For this method, we have also studied the influence of temperature and addition of Zn^{2+} , Al^{3+} and Co^{2+} ions to the electrolyte on electrochromic properties of nickel hydroxide films [37].

Papers devoted to deposition and study of films based on $\text{Ni}(\text{OH})_2$, rarely cover the influence of deposition time on electrochromic properties of films. Only papers [38, 39] present some data regarding the influence of deposition time, as a result, different film thicknesses, on coloration degree of the film prepared by sputtering. The data presented is for films that have a thickness of 0.017 - 1.08 μm , could be insufficient for a higher degree of coloration. As such aim of the present work is to determine the dependency of coloration and bleaching degree on deposition time for films deposited using cathodic template synthesis.

Experimental

All hydroxide films were prepared by cathodic deposition from aqueous 1M $\text{Ni}(\text{NO}_3)_2$ solution in presence of 5% wt. PVA as a template at room temperature and a current density of 0.625 mA/cm^2 . Deposition times were 10, 20, 40 and 80 min. The films were deposited onto nickel electrode [25, 34, 35] with working area of cm^2 , which was electrochemically polished in the following electrolyte: 520 g/L H_3PO_4 , 40 g/L CrO_3 , 550 g/L H_2SO_4 ; at current density of 0.5 A/cm^2 , temperature of 80 $^\circ\text{C}$, for less than 10 min.

$\text{Ni}(\text{OH})_2$ films were deposited using specifically designed diaphragm electrolyzer, presented on Figure-1. Thick nickel foil was used as the anode. Catholyte - 1M $\text{Ni}(\text{NO}_3)_2$ with the addition of 5% wt. PVA, anolyte - 1M KNO_3 .

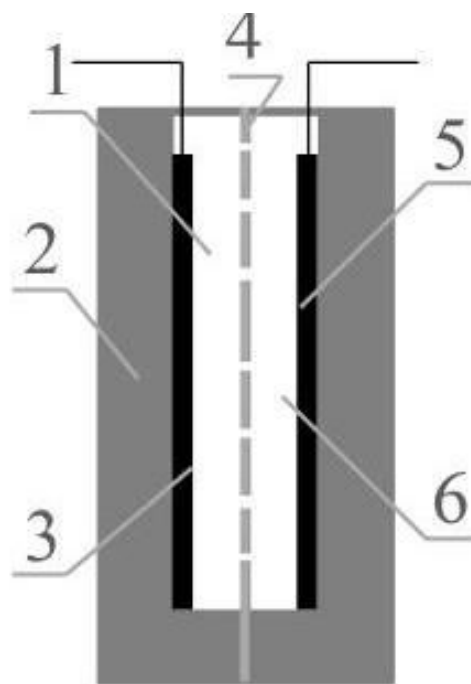


Figure-1. Schematic of electrolyzer for film deposition: 1 - Cathodic chamber; 2 - Electrolyzer (body); 3 - Cathode (polished Ni); 4 - Low-permeability diaphragm and U-shaped gasket; 5 - anode Ni; 6 - Anodic chamber.

Film morphology was studied by means of Scanning Electron Microscopy (JEOL JSM-6510LV) and Atomic Force Microscopy (NT-MTD «NTegra»). Film structure was analyzed by means of X-ray diffraction analysis, using DRON-3 diffractometer with monochromatic Co radiation.

Electrochemical and electrochromic properties of samples were studied using specifically designed cell (pic. 2). Electrochemical properties were studied by means of cyclic voltammetry with simultaneous recording of optical "coloration-bleaching" curves. Measurements were taken using potentiostat Ellins P-8 and ADC E-154. The ADC was used to record signal from sensors that registered a change in optical properties of the films during cycling, as



shown in Figure-2. Cycling parameters: potential window 0 - 725 mV (vs NHE), scan rate 1 mV/s. Electrolyte 0.1 M KOH, reference electrode - Ag/AgCl (KCl sat.), counter-electrode - nickel foil. The coloration degree was used as a criterion for evaluation properties of prepared nickel hydroxide. This value was calculated from "coloration-bleaching" curves, as a difference between transparency in bleached and colored state of the films.

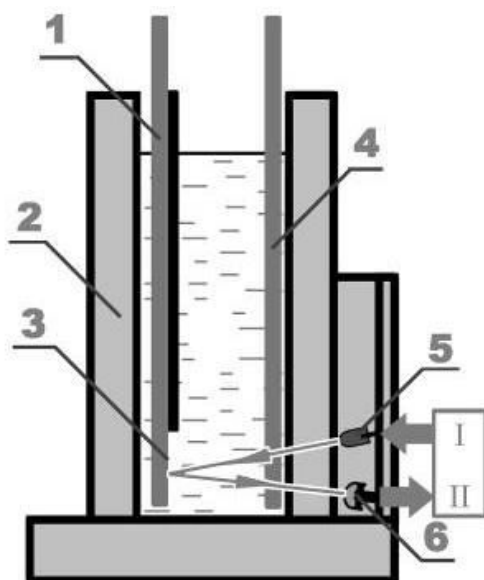


Figure-2. Cell for electrochemical and electrochromic tests: 1 - working electrode; 2 - cell's body; 3 - a working area of the electrode; 4 - U-counter electrode; 5 - LED; 6 - photoresistor; I - stabilized voltage input; II - signal output to an analog-to-digital converter.

RESULTS AND DISCUSSIONS

Morphology and structure

In order to determine the morphology of prepared samples, the SEM and AFM images of films deposited for 10, 20, 40 and 80 min have been recorded. For comparison, such images were also recorded for nickel substrate without $\text{Ni}(\text{OH})_2$ film. It is known, that surface morphology of deposited non-metallic films with thickness over 1 μm , is different from those of substrate. Deposition of nickel hydroxide films using cathodic template synthesis results in the formation of composite [6], which should differ from substrate morphology even more. Preliminary analysis of SEM and AFM images of films deposited at a different time has proved this hypothesis and revealed that all deposited films are uniform with a similar surface morphology that is different from that of the substrate. As such, the further discussion is focused on film deposited for 80 min, SEM and AFM images of which and nickel substrate are shown in Figures 3 and 4.

SEM images of nickel substrate (Figure-3a and 3b) reveal relief uniformity, however, some microbumps are present (Figure-3a). After the film was deposited for 80 min., the surface became more uniform and leveled (Figure-3c and 3d). As such, nickel hydroxide film with template also serves as a leveling agent.

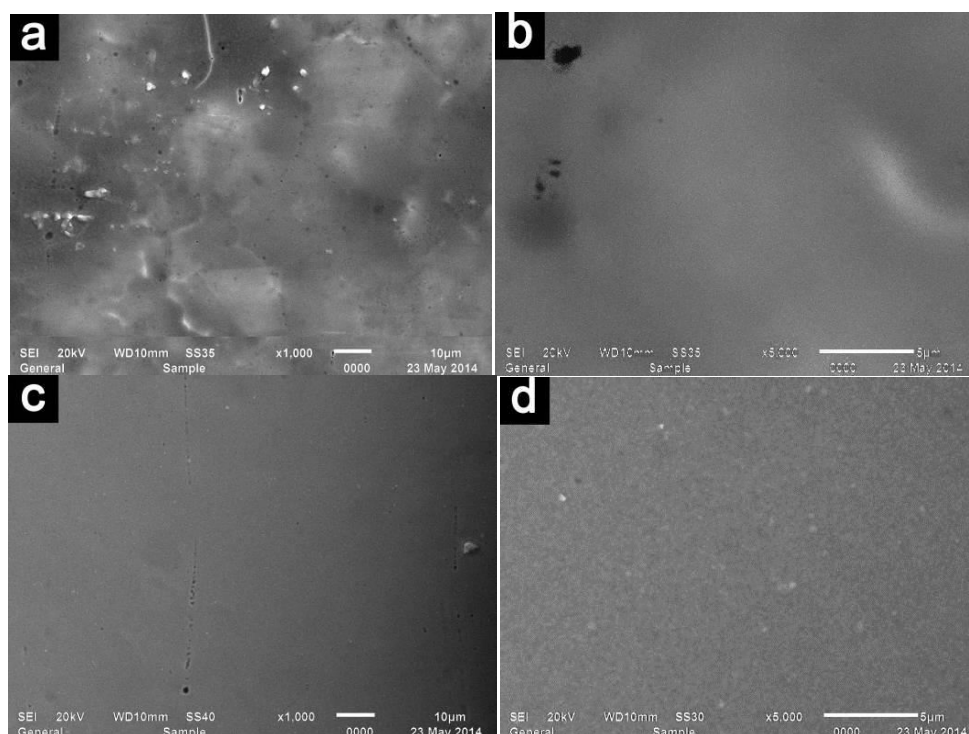


Figure-3. SEM images: a, b - nickel substrate; c, d - substrate with a film deposited for 80 min.



Analysis of AFM images (Figure-4) has revealed that nickel substrate has microbumps from 100 to 500 nm in diameter (Figure-4 b), and have a height of about 160 nm - Figure-4a. It should be noted, that bumps have a smooth and convex shape (Figure-5a, which is a 3-d visualization of Figure-4b). Such shape is a result of mechanical treatment of nickel, followed by smooth during electrochemical polishing. For nickel hydroxide film deposited for 80 min. the average bump height is 180 nm (the later doesn't include single peaks 350 nm high -

Figure-4c), which is almost exactly as for substrate. This illustrates uniformity of the film deposited from solution with polyvinyl alcohol as a template. However, the diameter of microbumps is significantly smaller 30 - 100 nm (Figure-4d), their shape is also different. The difference in shape is shown in detail in Figure-5a and 5b, which is a 3-d visualization of Figure-4b and 4d. It can be assumed, that bumps in Figure-5b are polycrystals of nickel hydroxide.

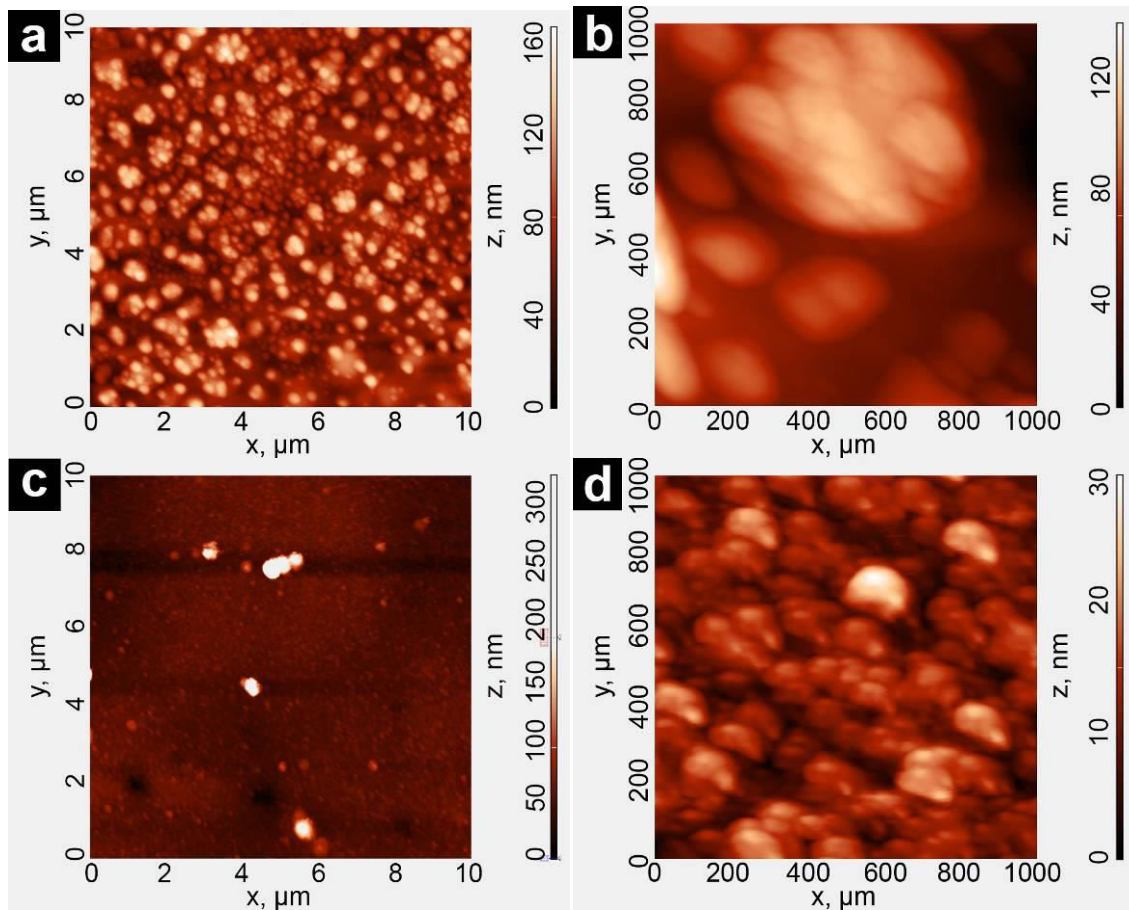


Figure-4. AFM images: a, b – nickel substrate; c, d – substrate with a film deposited for 80 min.

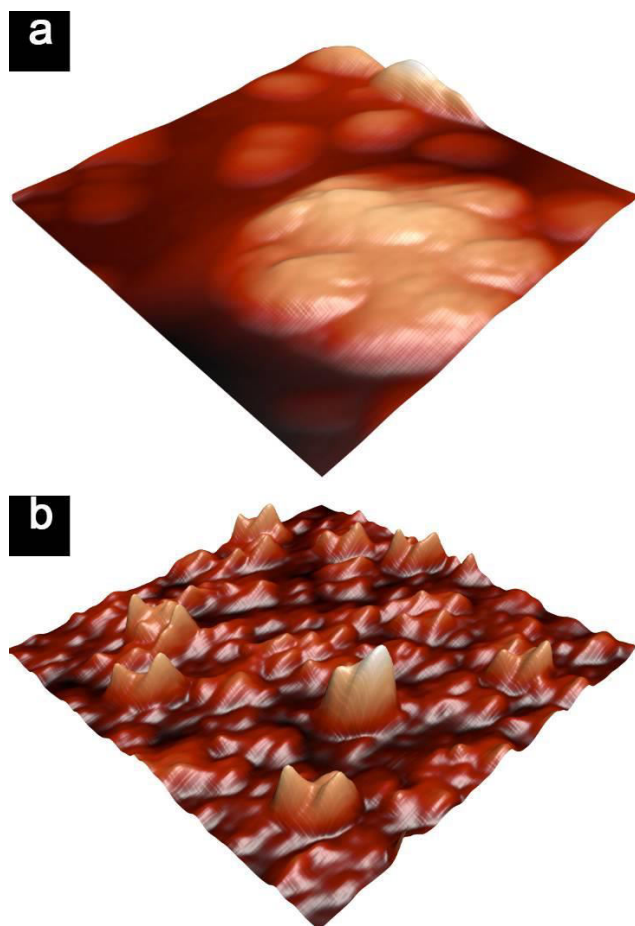


Figure-5. 3-d visualization of surface: a - substrate (Fig. 4b) and b - substrate with a film deposited for 80 min (Fig. 4d).

It should be noted, that formation of uniform deposit is important for electrochromic devices, as uniform thickness of would directly affect transparency and cause less light distortion when the film is deposited on the transparent substrate.

In order to evaluate the structure deposited films, the samples were subjected to XRD analysis. Because separation of the nickel hydroxide film from the substrate proved to be problematic, it was decided to conduct XRD analysis of films deposited onto the substrate.

It is known, that surface of metallic nickel contains some amount of oxide and hydroxide compounds, which can affect the XRD pattern [40], so in order to distinguish between peaks of the film and substrate, an XRD pattern of bare nickel with the film was also recorded. Figure-6 shows XRD patterns of bare nickel substrate and with a film deposited for 80 min (XRD, patterns of the films deposited for 10, 20 and 40 min, show similar X-ray amorphous structure and are not shown in Figure-6).

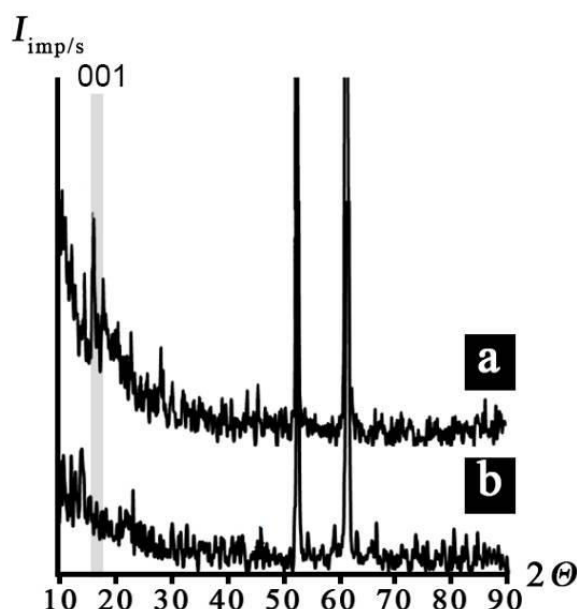


Figure-6. XRD patterns: a - substrate with a film deposited for 80 min; b - nickel substrate.

Few conclusions can be drawn from analysis of obtained XRD patterns. First, the surface indeed contains some amount of oxide-hydroxide compounds. Two strong peaks at 52° and 62° correspond to metallic nickel. The $\text{Ni}(\text{OH})_2$ film, deposited for 80 min, has low crystallinity (almost X-ray amorphous) and has a structure similar to $\alpha\text{-Ni}(\text{OH})_2$ as the only peak is located at 13°, which is characteristic of 001 plane of $\alpha\text{-Ni}(\text{OH})_2$. It can also be assumed that deposit has a large number of the defect and likely contains significant amounts of structural water.

Electrochemical and optical properties

All prepared films were subjected to potentiodynamic cycling with simultaneous recording of optical properties. Figure-7 shows cyclic voltammograms of films deposited for 10, 20, 40 and 80 min. Comparison of cyclic voltammograms reveals that with increasing deposition time the current of oxidation and reduction peak increases. In series 10 - 20 - 40 - 80 min peak current increases 0.017 - 0.019 - 0.028 - 0.053 A/dm^2 (anodic peaks) and 0.013 - 0.02 - 0.023 - 0.06 A/dm^2 (cathodic peaks). Capacities calculated for reduction process (5-th cycle) of electrochromic films in deposition time series are 0.039 - 0.062 - 0.044 - 0.140 $\text{mA}\cdot\text{h}$. It is also seen, that peak current increases with longer deposition time. This can be explained by the larger amount of active material ($\text{Ni}(\text{OH})_2$) at longer deposition time.

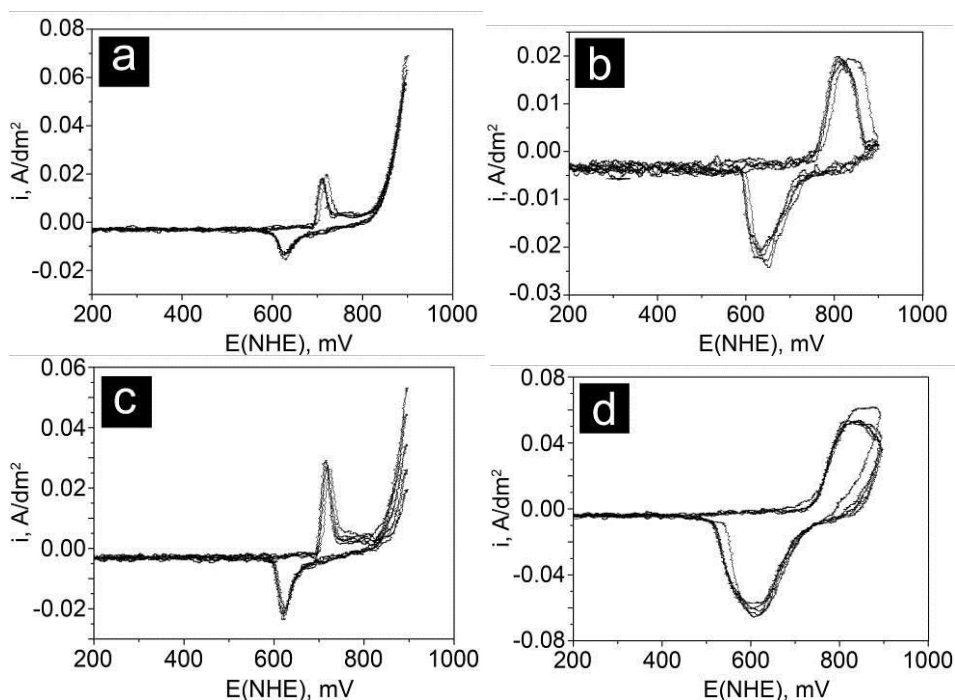


Figure-7. Cyclic voltammograms of the films: a - deposited for 10 min; b - deposited for 20 min; c - deposited for 40 min; d - deposited for 80 min.

Despite that deposition time was incised by two times of the previous duration, the peak current values do not exactly follow this tendency. This is likely explained by partial inhomogeneity of films.

It should be noted that peak reduction peak potential volutes are within a narrow range of 610 - 625 mV. On the other hand, the potential values of oxidation peaks lie within a wider range of 720 - 820. Currently, there is no clear explanation for this fact, which requires additional studies.

Figure-8 shows optical properties of the films deposited for 10, 20, 40 and 80 min during potentiodynamic cycling. As expected, longer deposition times resulted in films with high coloration degree. It obvious, that longer deposition time results in films with thicker films, which in turn affects maximum coloration

degree. It was also discovered, that different deposition times lead to some difference in form of coloration-bleaching curves. The most notable difference is observed for the film deposited for 80 min. The coloration part of the curve (during the positive potentiodynamic scan), shows a slope at the beginning, which is followed by a sharp drop to the minimal transparency value. However, it then rises and falls again (which results in W-like shape), and only then the bleaching process starts. It should be noted, that the apex of mini-peak corresponds to the utmost positive potential value on cyclic voltammogram. This is likely related to phase composition of oxidized form and will be studied separately because the form of the bleaching-coloration curve and factors influencing it is very important for the operation of the electrochromic device.

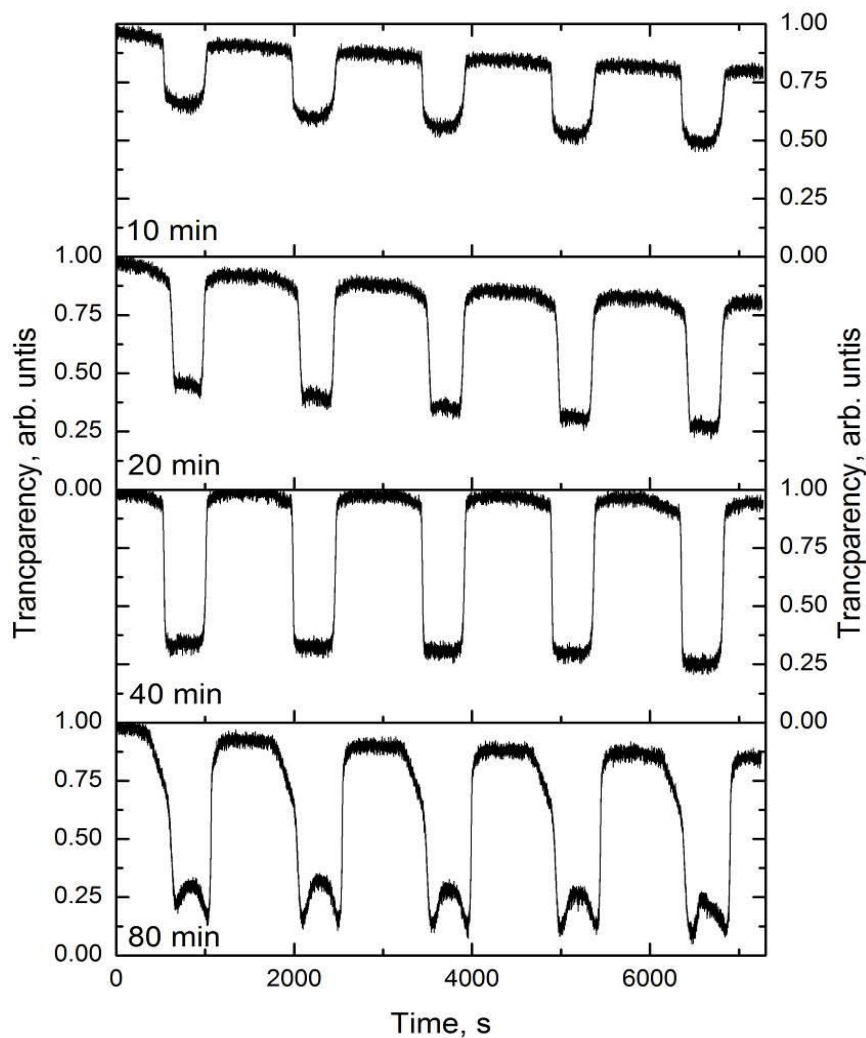


Figure-8. Coloration-bleaching curves of films deposited at different deposition times.

All film samples switched to the colored state during cycling, however, their bleaching was incomplete. In our opinion, the incomplete bleaching is related to the nickel substrate, as it can also undergo a color change, as shown in the literature [6]. When comparing properties, it is interesting to analyze how the difference between transparency in the colored and bleaching state (i.e. transparency change of the film) would change with cycle number. As such, the curves presented in Figure-8 were subject to additional analysis. The transparency change

values for each cycle taken from curves in Figure-8 were used for plotting histogram Figure-9. Field "Coloration" represents transparency change (i.e. coloration degree) during coloration, from mid-point in the bleached state to mid-point in the colored state. The value in "Bleaching" field represents transparency change during bleaching, from mid-point in the colored state to mid-point in the bleached state. "Average" represents an averaged value for all cycles for a given group.

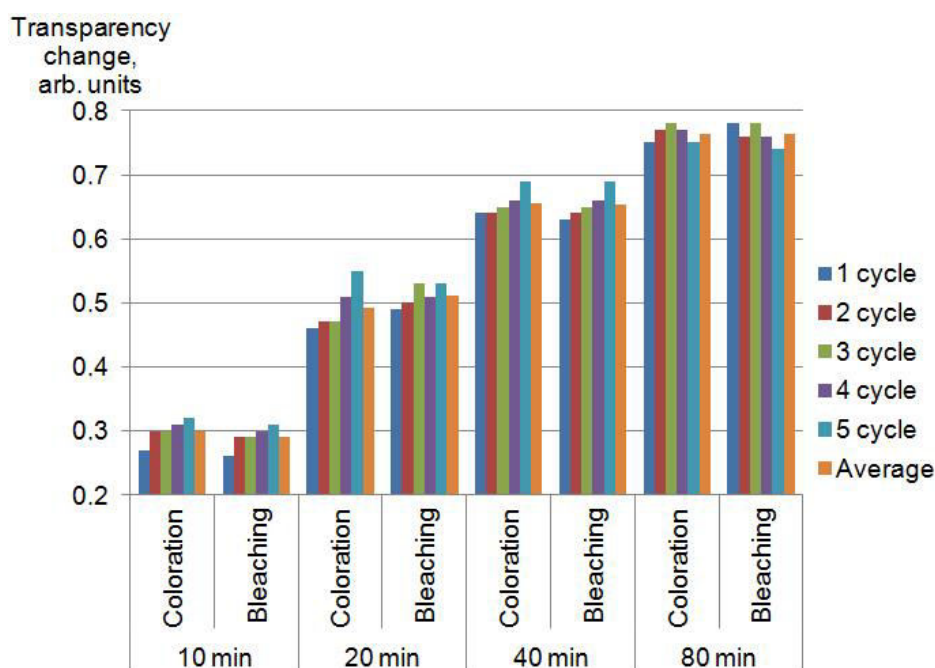


Figure-9. Transparency change with cycle number of films with different deposition times.

Analysis of obtained data allows drawing few conclusions. First, the values of transparency change during coloration and bleaching for each given films are almost the same. This indicated that reversibility of coloration-bleaching is very high and is close to 100%. Second, for film deposition with cathodic template synthesis, the optimal deposition time appears to be within 40 to 80 min. This results in maximum transparency change during coloration and bleaching. From presented data, it also follows that further increase of deposition time

is not rational, as the gain of average coloration depths not significant. For a film deposited for 10 min the average coloration degree is equal to 0.3 (Figure-9). At deposition time of 20 min, the coloration degree is equal to 0.5. The two times increase in deposition time results in an increase of coloration degree of about 70%. Further increase of deposition time to 40 min, the transparency change is 0.65. In this case, the gain is about 31%. At deposition time of 80 min, the average coloration degree is 0.75, with a gain of 17%, over the film deposited for 40 min (Figure-10).

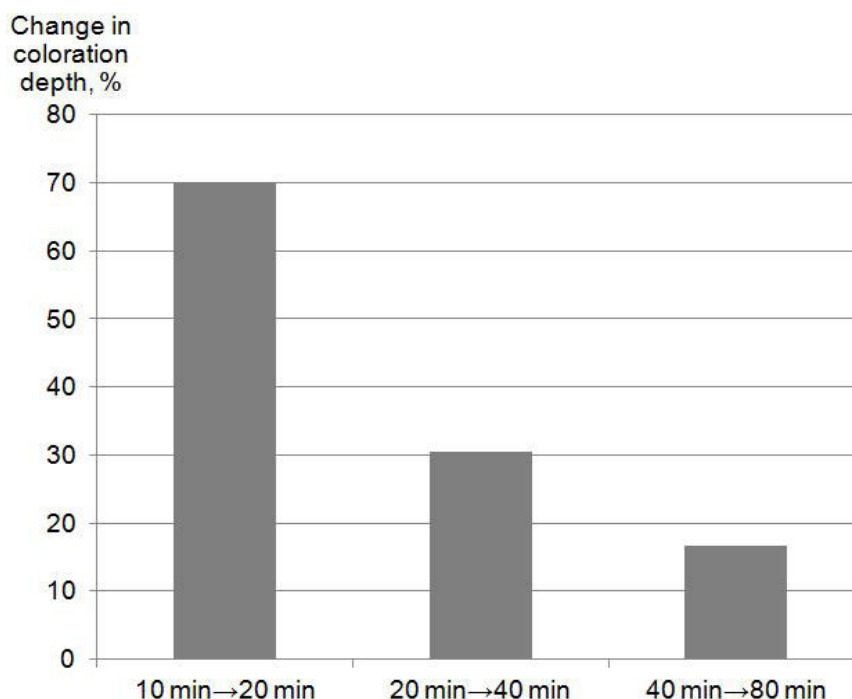


Figure-10. Change in coloration depth for different deposition times.



As such, a further increase in deposition time would lead to consumption of electricity and reagent, without a significant gain in the bleaching-coloration degree of the resulting film. This fact likely indicated that at a deposition time of 80 min the transparency change is defined primarily not by film thickness but by optical properties of components in the oxidized film.

CONCLUSIONS

The influence of deposition time on electrochemical and electrochromic properties $\text{Ni}(\text{OH})_2$ based films deposited using cathodic template synthesis have been studied. By means of SEM and AFM, it was revealed that deposited films are uniform, the morphology does not depend on surface morphology of substrate; the size of microbumps is 30-100 nm in diameter, and their high is below 180 nm. By means of XRD analysis, it has been established that films have a structure of $\alpha\text{-Ni}(\text{OH})_2$ with very low crystallinity and a larger number of structural defects. Electrochemical and electrochromic properties of the deposited films have been studied by means of cyclic voltammetry with simultaneous recording of optical properties. Analysis of cyclic voltammograms revealed an increase of cathodic and anodic peak current values with increasing deposition time, which correlated with the increased amount of nickel hydroxide in the film. Analysis of coloration-bleaching curves revealed high reversibility of the films. It was also discovered, that in series of deposition times 10 – 20 – 40 – 80 min, the coloration degree was 0.3 – 0.5 – 0.65 – 0.75, which results in 70% – 31% – 17% gain with increasing deposition time. The optimal deposition time for electrochromic films at a current density of 0.625 mA/cm^2 lies within 40-80 min, and a further increase of deposition time is irrational.

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