



ADVANCED ELECTROCHROMIC Ni(OH)₂/PVA FILMS FORMED BY ELECTROCHEMICAL TEMPLATE SYNTHESIS

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ABSTRACT

Electrochromic nickel hydroxide film has been prepared for the first time, using electrochemical template synthesis with polyvinyl alcohol (PVA) as template. Such advanced Ni(OH)₂/PVA composite film has improved adhesion to substrate and can be potentially used for manufacturing flexible electrochromic devices. Films obtained by template cathodic deposition can be stored in a dry state without morphological changes which allows for optimization of manufacturing of complete devices. The optimal concentration of polyvinyl in electrode position solution has been found 5% wt. It has been demonstrated that polyvinyl forms nanosized 3-D matrix on substrate surface which promotes formation of X-ray amorphous nickel hydroxide and is incorporated into the film. It has been established, that at optimal current density 0.625 mA/cm² the deposition rate is 3.87 μm/h. By simultaneously recording cyclic voltammograms and colorization curves high electrochemical and optical properties of films prepared using template synthesis with PVA have been demonstrated, with coloration degree of up to 80%. Significant effect of drying temperature on electrochemical and optical properties of Ni(OH)₂/PVA composite films has been demonstrated. Low drying temperature (20° C) results in films with high electrochemical activity and coloration degree. At 90° C a drop in colorization degree has been observed.

Keywords: nickel hydroxide film, template electrochemical synthesis, polyvinyl alcohol, electrochromic properties, smart windows.

1. INTRODUCTION

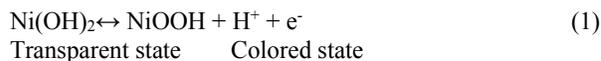
Electrochromism is a reversible phenomenon leading to materials colorization and bleaching under polarization current. Electrochromic effects, typical of some metal oxides or hydroxides [1-11], appear upon either oxidation or reduction reaction. Thereby electrochromic materials are usually divided in two main groups: cathodic, e.g. Nb₂O₃, V₂O₅, MoO₃, WO₃, and anodic, e.g. CoO_xH_y, RhO₂, IrO_xH_y, NiO_xH_y. A most common feature of these materials is the electrochemical mechanism involving coupled insertion/extraction of electrons and ionic species. Polymers like polyaniline, can be also used as electrochromic materials.

The key issues for the development of effective electrochromic devices are good handling, high colorization ability (high contrast between the colored and transparent states), reversibility of the colorization/bleaching electrochemical process and effective color maintenance, i.e. high coloration efficiency. A further drawback hindering the development of this technology is the need to develop materials which can be easily deposited as homogeneous films conductive substrate.

A typical electrochromic cell correspond to a layered structure consisted of stacked glasses, transparent conductive substrates, electroactive materials, electrolyte and ion-conductive layers enhancing ion exchange between them. Usually, both electrodes exhibit electrochromic features though one electrochromic electrode is sometimes replaced by a transparent ion-

storage layer. All elements of the electrochromic cell must exhibit high optical transparency. In the specific case of "Smart" mirrors with variable reflective ability, one glass is replaced by a mirror.

For many years, nickel (oxy) hydroxide [12-15] has been considered as a perspective electrochromic electrode material. The electrochemical process with colorization is assumed to follow:



The electroactive material is usually synthesized in the reduced form. Different methods can be used for obtaining nickel hydroxide thin films: electrochemical deposition from Ni salts solution, dip-coating, vacuum evaporation, pulsed laser or chemical vapor deposition, spray pyrolysis, sol-gel process and chemical bath deposition [16-18]. However the electrochemical deposition appears to be more efficient, since the thickness and structure of the films can be controlled by the current density and electrolyte composition.

Both anodic and cathodic electrochemical deposition of nickel hydroxide have been previously reported [19-30]. Anodic-deposition is based on the preliminary decomposition of nickel ammonia complexes by anode acidifying the electrolyte [29, 30]. Cathode deposition consists in the precipitation of nickel hydroxide from solutions of nickel salts with high solubility e.g. sulfate, chloride and nitrate. Different initial pH has been



used, depending on the electrolysis condition. Independently on the electrochemical condition, these previous studies highlight the main drawback of poor adhesion and mechanical properties of the deposited film. Thus, in [19] mentioned "The precipitate formed in the cathode chamber was filtered.... It is clear, that cathodically formed $\text{Ni}(\text{OH})_2$ peels off due to weak adhesion. Also "The mechanical rigidity was poor, and the films easily flaked off the substrate" [24]. "In the light micrograph an electrochemically precipitated $\alpha\text{-Ni}(\text{OH})_2$ film are shown. The surface visibly cracked when the film was dried." [31]. Surface cracking is a result of high internal mechanical stress of the film [32]. Especially, low adhesion and high internal mechanical stress of the film lead to visible cracks in thick films of nickel hydroxide [19, 24, 31, 32]. These facts do not allow depositing flexible electrochromic films. It is clear that without any suitable post-electrodeposition treatment or additives, the electrodeposited films of pure $\text{Ni}(\text{OH})_2$ do not exhibit the proper features for electrochromic application. First, to solve this issue, several authors increased the temperature of the thermal treatment in order to convert the pristine $\text{Ni}(\text{OH})_2$ into Ni_xO_y oxide, thus expecting to improve the hardness and adhesion of the film. But such high treatments are expensive at the industrial scale and, most important, resulted in the degradation of the electrochromic properties [22, 26]. Others have chosen to skip the drying steps at all [27].

This way is quite irrational because it is impossible to set up the final electrochromic device without electrode drying. In other words, the process of deposition and drying of $\text{Ni}(\text{OH})_2$ film cannot be considered as separate stages of the device production, they are strictly tied to the previous and next operations e.g. preliminary treatment of conducting substrate, washing, assembling with the counter-electrode, current lead pasting, etc. In such case, inability to dry electrode will be a great inconvenience for real production, not only because of the technical issues related to the storage in aqueous media but also of the stability of electrochromic properties [33].

One of the potentially effective ways for solving this issue is to use electrochemical template synthesis. Template synthesis is widely used for synthesis of different type of solids with controlled porosity and morphology. For instance Tan et al. [41] reported a micelle-templated mesoporous nickel hydroxide film obtained from diluted surfactant solution. Needless to say that in such a case, the extraction of the liquid template after deposition yields a porous film which is not suitable for electrochromic application. Since our goal is to increase the film mechanical and adhesive properties, our assumption is to use a template that would form a composite film made of a polymeric network embedding the $\text{Ni}(\text{OH})_2$ crystallites and that would remain in the film after drying and temperature treatment. For template synthesis from aqueous solutions, water soluble high molecular compound must be used. The most interesting substance for this purpose is likely the polyvinyl alcohol (PVA) which is widely used as a porosity controlling

agent template for synthesis of mesoporous alumina [36], hydroxyapatite crystallites (with sodium dodecyl sulfate) [37], mesoporous MFI zeolite (as a secondary template) [38], nanosized MgO [39], 3D-structured macroporous oxides and hierarchical zeolite for catalysis purposes [40], polypyrrole (PP) network (for ammonia gas sensor) [42]. In the later, a composite matrix PVA film was formed. It also has been shown by Gu *et al.* [43] that the addition of PVA improves the adhesion of anodized aluminum oxide onto indium-tin oxide surface.

In the present work, we aim to investigate the electrochemical template synthesis of $\text{Ni}(\text{OH})_2$ /PVA composite films with improved mechanical and adhesion features while maintaining good electrochromic characteristics. The influence of the electrolyte composition, the electrochemical deposition conditions and drying temperature on the structure, electrochemical and electrochromic properties of the so-obtained nickel hydroxide/PVA film is reported [44, 45].

2. EXPERIMENTAL

2.1 Formation of nickel hydroxide films.

Polished nickel foils were used as substrate for all the deposited nickel hydroxide/PVA film, as reported in [27]. The interest of using such a substrate is dual. First, nickel foils have higher conductivity, i.e. compared for instance to ITO substrates. This property is expected to yield a more homogeneous distribution of the current density at the substrate surface and, thus, a more homogeneous nickel hydroxide deposit. Second, polished nickel substrate allows higher sensibility when recording the optical parameters of the electrochromic film, thanks to its higher light absorption due to the double ray crossing the $\text{Ni}(\text{OH})_2$ layer (light source \rightarrow $\text{Ni}(\text{OH})_2$ film \rightarrow mirror-like Ni substrate \rightarrow $\text{Ni}(\text{OH})_2$ film \rightarrow light detector).

Electrochemically polished nickel foil substrates have been prepared under the following conditions: electrolyte with 520 g/l H_3PO_4 , 40 g/l CrO_3 , and 550 g/l H_2SO_4 ; current density of 50 A/dm^2 ; temperature 80 °C, treatment time up to 10 min.

All films of nickel hydroxide were electrochemically deposited at 20°C during 80 min in a diaphragm cell with 1M $\text{Ni}(\text{NO}_3)_2$ and 1 M KNO_3 in the cathode and anode space respectively. Pure $\text{Ni}(\text{OH})_2$ and composite $\text{Ni}(\text{OH})_2$ /PVA films were deposited at different current densities: 0.313, 0.625, 1.25, 2.5 and 5, mA/cm^2 . A nickel foil was used as anode. Polyvinyl alcohol (PVA) was used as non-extractable template. Investigated PVA concentrations were 1, 3, 5, 7 and 10 wt %. After deposition, the samples were rinsed by distilled water during 1 hour by immersion and then dried at 20°C or 90 °C during 24 hours.

2.2 Characterization

The preliminary testing of the films obtained with templates was carried out by optical observation, in order to assess the transparency and homogeneity, i.e. the absence of cracks. The optical observation was carried out



in transmitted light mode with a Bresser digital microscope (Germany) with a magnification up to 350. The film morphology was also investigated by SEM and ASM, using a PEMMA 120-02 scanning electron microscope (Russian Federation) and atomic-force microscope NT-MTD «NTegra» (Russian Federation). For recording SEM images, each sample was covered with a thin film of platinum few nm thick. The crystallographic structure was analyzed as a function of the deposition current density by XRD with a DRON-3 diffractometer (Russian Federation) (Co-K α radiation, range 10-90° 2 θ , step resolution 0.1°2 θ , acquisition time per step 1 s). Chemical composition was studied by EDX analysis with a Hitachi S4500 microscope (Japan).

Electrochemical and optical properties were investigated under cyclic voltammetry conditions by *in situ* colorization-bleaching measurements. A schematic representation of the experimental set-up is reported in Figure-1. A “Elins” P-8 potentiostat (Russian Federation) was used for the electrode potential control. Optical measurements were carried out with an analog-to-digital E-154 device. The reference electrode was Ag/AgCl (KCl sat.). The cycling potential range was [+200 mV; +750 mV] vs. NHE. The light source was a non-monochromatic white light emitted diode powered by a constant voltage. The brightness of the reflected beam was recorded by means of a light detector connected to the analog-to-digital device. A light resistor with optical system was used as light detector.

3. RESULTS AND DISCUSSIONS

3.1 Optical and structural characterization of the reference materials obtained without template

For formation of advanced composite Ni(OH)₂/PVA film, optimization of the conditions of the nickel hydroxide deposition has been carried out. For this, influence of the deposition current density on structure, surface morphology and transparency of pure Ni(OH)₂ film has been investigated.

All the samples which were synthesized from Ni(NO₃)₂ solution without template are observed to flake off during drying. Figure-2 compares optical images from the same sample (deposited at 0.625 mA/cm²) before and after drying at 20° C. A network of cracks can be clearly observed after drying. Light refraction at the edges is a further evidence of the presence of Ni(OH)₂ flakes that lost contact with substrate. The experimental conditions used here are similar to those used by others [24, 31, 32] and confirm that pure nickel hydroxide films do not stick well onto the substrate and exhibit high internal mechanical stress.

XRD patterns reported in Figure-3 for the films obtained at different deposition currents, are characteristic of badly crystallized materials. All patterns correspond to poorly ordered α -phase and can be indexed according to the rhombohedral system with the P3 structural type (see [34]). The structure can be depicted with a hexagonal cell [31], where the $d(001)$ distance leads to the value of the

interlayer distance which is observed to increase with the deposition current, from 5.5 ± 0.5 to 8.5 ± 0.5 Å. This behavior can be explained by the local concentration of OH⁻ at the electrode surface during the synthesis, which depends both on the current density and on the thickness of the hydroxide film already deposited. The complex interplay between these two parameters leads to better defined α -phases containing water, nitrate and carbonate anions in the interlayer space when the current density is higher. At the lower current density, even less crystallized materials are obtained, whose structural disorder results from a predominantly α -type framework interstratified with a lower percentage of β -type motifs. According to the work of Rajamathi *et al.* [35], the β -like motifs percentage could approach 50 % for the deposit obtained at the lower current, 0.3125 mA/cm². It should also be noted that low crystallinity could arise from the turbostratic disorder often affecting lamellar materials *i.e.* the random rotation and/or translation of the individual -O-Ni- layers relative to each other which leads to the selective broadening of the non- $hk0$ peaks.

Optical images of these pure Ni(OH)₂ film deposited without template that peeled off from the substrate, are reported in Figure-4. It can then be clearly observed that the increase of current density leads to the decrease of the film transparency because of the appearance of particles agglomerates (see Figure-4e and 4f). Such a phenomenon is presumably due to the local OH⁻ concentration during deposition which increases with the current density. At high currents, the early stages of the nickel hydroxide deposition process are faster, resulting in heterogeneous films (*i.e.* high surface roughness). Once the hydroxide deposit attains a certain thickness, the electrode surface becomes less conductive and the OH⁻ formation rate is slower. The precipitation process then results in a more homogeneous films.

Proof of this mechanism could be found in the fact that roughness always appears at the film side in contact with the Ni substrate. Therefore, the deposition process carried out at 0.625 mA/cm² corresponds to the best compromise between good transparency and relatively short deposition time and hence will be used in the following experiments. For comparison, it should be pointed out that 0.625 mA/cm² in our experimental conditions corresponds to experiments at 0.3 mA reported in [20].

It should be noted that weak adhesion to the substrate and cracks emergence after film drying in all the above experiments has been observed, thus confirming the previous studies reported in the literature.

3.2 Studying template concentration

Different concentrations of PVA have been studied. Addition of 1 and 3% wt PVA to Ni(NO₃)₂ solution allowed to obtain homogeneous and transparent films but they still not adhere enough on the Ni substrate. 5 % wt PVA addition is found to be the optimum for both optical and adhesion properties. At higher concentration of PVA, solution's viscosity becomes too high and affects



film homogeneity.

3.3 Investigation of the nickel hydroxide/PVA composite film samples with 5 % wt template addition

For understanding the influence of PVA addition as a template in electrolyte on structure, the XRD patterns of Ni(OH)₂/PVA films on substrate were obtained. All earlier XRD patterns was obtained for flakes Ni(OH)₂ precipitated without template, since it was easily separated from substrate. However, in case of precipitation in the presence of 5% PVA, adhesion of films was extremely high and internal mechanic stress was low, so the film could not be peeled off easily. Therefore, XRD experiments were carried out while the films were remained attached to the substrate (Figure-5a). For comparison, XRD pattern of the substrate was also recorded and showed two high peaks at 52 and 62° characteristic of the Ni metal (Figure-5b). It can be seen from Figures 3 & 5a that films deposited with and without PVA exhibit very different behaviors since it is clear that the template formation yields amorphous material (Figure-5a). This result is based on the mechanism of the template synthesis: when substrate immerse to electrolyte, template forms the 3D network on the substrate surface. During electrolysis Ni(OH)₂ nanoparticles are growing in the cell of this 3D network, as described in [40] and visualized in Figure-6. Figure-7 compares the surface morphology of two films, both deposited from 1 M Ni(NO₃)₂ solution with 5% PVA but at different current densities and different deposition time, i.e. 0.625 mA/cm² during 80 minutes (Figure-7a) and 1.25 mA/cm² during 40 minutes (Figure-7b). The film surface is flat though showing cracks. It can be assumed that this morphology is caused by local mechanical stress occurring during the drying step.

Assuming that crack depth corresponds to film thickness, the thickness of film deposited at 0.625 mA/cm² can be calculated from SEM image, based on representation in Figure-8 using following equation:

$$v = b \cdot \operatorname{tg}(\beta) \cdot \frac{60}{t} \quad (2)$$

where b is the shadow length, β the beam angle and t the electrode position time. Providing that $b=3 \mu\text{m}$, $\beta=60^\circ$ and $t=80 \text{ min}$, equation (2) leads to $v=3.87 \mu\text{m}\cdot\text{h}^{-1}$.

The deposition rate calculated using equation (3) from [21], under our experimental conditions, is $3.16 \mu\text{m}\cdot\text{h}^{-1}$. As a result we can ascertain good corresponds under both values. The minor difference can be explained by the presence of PVA inside the composite film, as attested by EDX analysis reported in Table-1 (see the carbon % weight).

The AFM images of Ni(OH)₂ film deposited at 0.625 mA/cm² during 80 minutes are shown in figures 9a and 9b. It can be seen that the surface of our nickel hydroxide film is rather rough. The maximal roughness height is about 110 micrometers.

It is well known that nickel foil surfaces are

covered by a thin oxide layer (10-30 nm). In alkaline media, it forms nickel (oxy) hydroxides which can contribute to the electrochromic behavior of the electrode. In order to verify the contribution of the nickel substrate to the electrochemical and colorization ability of the electrode, optical measurements coupled to cyclic voltammetry have been carried out on the pristine substrate (Figure-10a). The electrochemical and optical activities of the hydroxide surface layer are very low. Only a weak, gradual darkening can be observed (see Figure-10b). It can then be concluded that the contribution of the substrate is negligible when studying the electrode with the electrochemically deposited hydroxide/PVA film.

Electrochemical & electrochromic properties of the nickel hydroxide/PVA films, electrodeposited by template synthesis and dried under different temperatures, are reported in Figures 11 and 12. Both figures show the behavior of the samples obtained from 1 M Ni(NO₃)₃ solution with 5% weight PVA and deposited under 0.625 mA/cm². Figure-11 corresponds to the sample dried at 90 °C during 24 h and Figure-12 to the sample dried at 20°C during 24 h.

Both films exhibit higher electrochemical activity than that of the substrate alone (compare Figures 11a and 12a to Figure 10a). Most important, the sample dried at 20 °C exhibits a higher electrochemical activity, i.e. current of the charge and discharge peaks is 4.2 mA and 3.9 mA respectively (Figure-12a), than the samples dried at 90°C, i.e. the charge and discharge peaks equal 2.9 mA and 2.75 mA respectively (Figure-11a). It should be noted that the charge-discharge curves of the sample dried at 90°C shows no clearly defined charge peaks as compared with the sample dried at 20°C. Thus, it should be concluded the Ni(OH)₂/PVA film dried at 20°C shows a better optical response during electrochemical cycling, i.e. larger colorization depth (compare Figures 11b and 12b). However the sample dried at 90°C exhibits a larger colorization/bleaching reversibility. The sharp difference between the transparency plots of the samples dried at 90 and 20°C can be readily seen on Figures 11 and 12. For the sample dried at 90 °C, the shape of the optical change is almost perfectly rectangular. As for the sample dried at 20°C, despite the higher degree of colorization-bleaching change, the optical response shows dips after colorization and before bleaching (see Figure-12b). This effect is very interesting and requires a deeper investigation.

The different optical behaviors of the films dried at 20° and 90° C could be related to the influence of PVA on the morphology of the film. The EDX analysis attests the presence of PVA in the deposited film. It is therefore likely that the presence of PVA which is an insulating material significantly modifies the conductivity homogeneity of the film. The drying process at 90 °C may induce a (partial) sub-melting of the PVA sub-network which affects/reduces the open-cellular structure induced by the polymer template grid and, consequently, leads to a tighter encapsulation of the nickel hydroxide particles resulting in degradation of the film's conductivity. The other reason could be the partial dehydration of the



Ni(OH)_2 particles also leading to an overall decrease of conductivity.

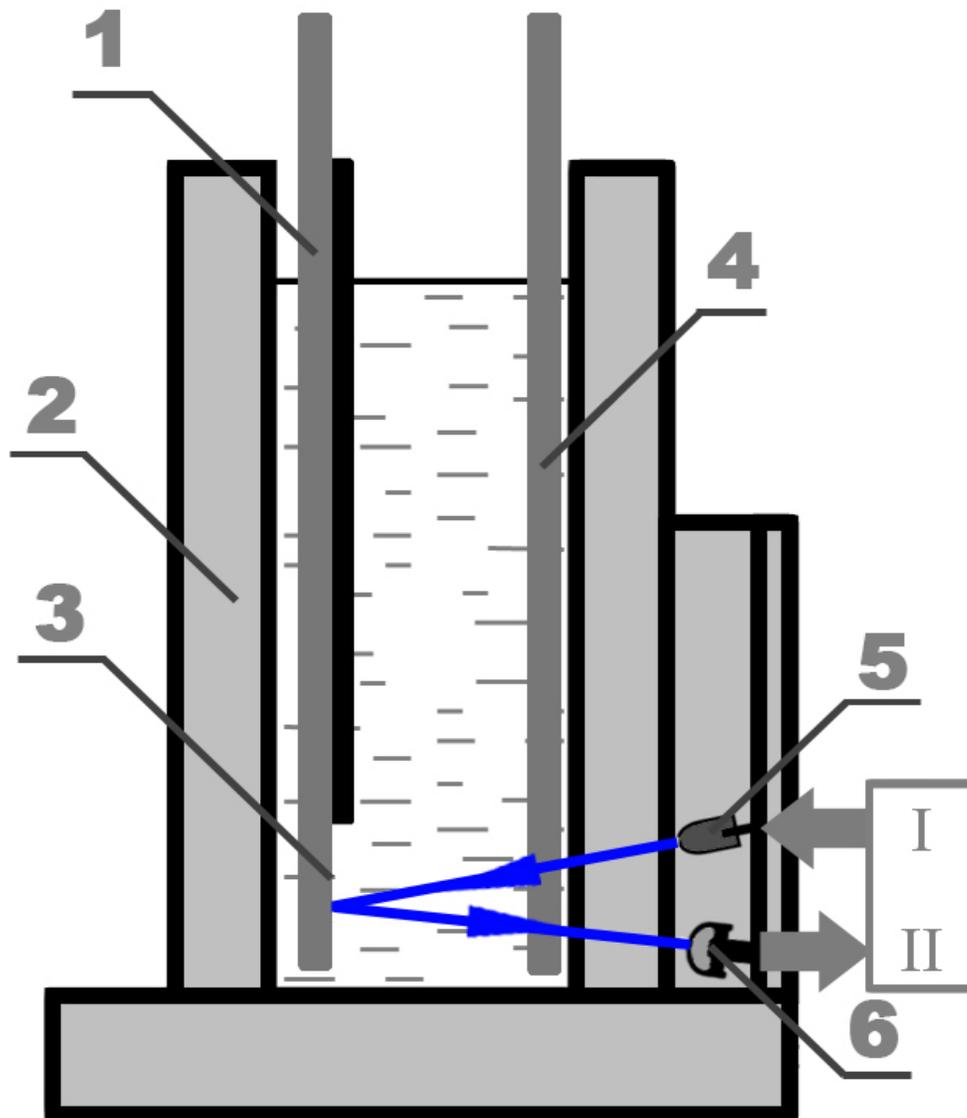


Figure-1. Scheme of the experimental cell for coupled electrochemical and optical measurements. 1 - the non-conducting coating with black color deposited on the working electrode; 2 - transparent cell case; 3 - the surface of the working electrode with electrochromic film; 4 - the counter electrode; 5- focused light source; 6 - photoresistor (I- input from stabilized power source; II - output to analog-to-digital device connected to PC). The reference electrode is not shown.

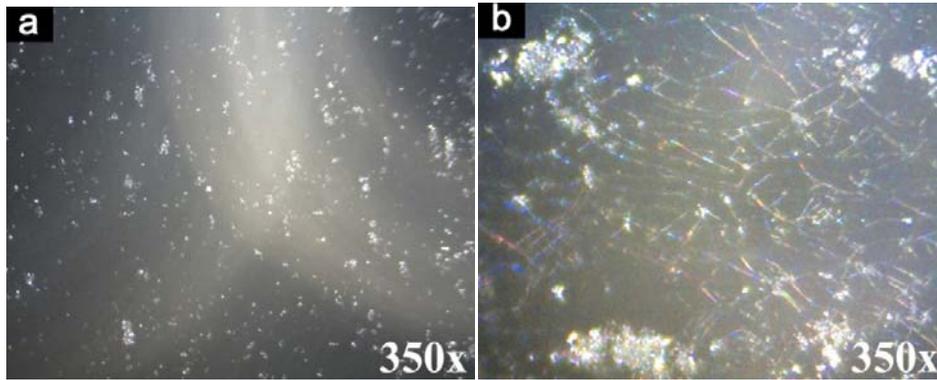


Figure-2. Optical images of $\text{Ni}(\text{OH})_2$ films deposited from $\text{Ni}(\text{NO}_3)_2$: (a) after deposition; (b) after drying.

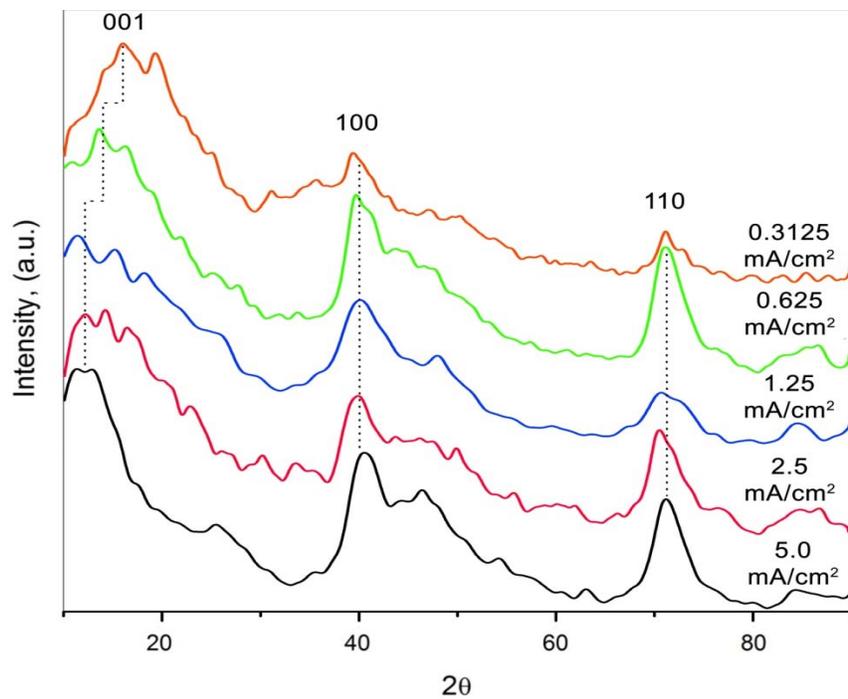
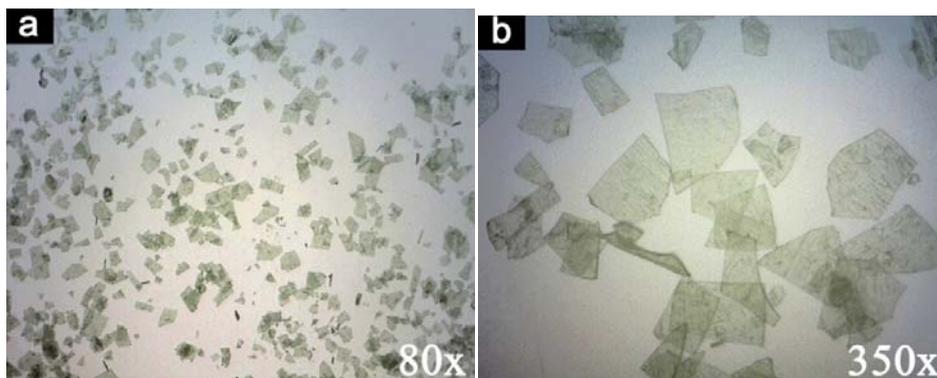


Figure-3. XRD patterns of non-doped nickel hydroxide films electroplated under different current densities (as indicated in the figure).



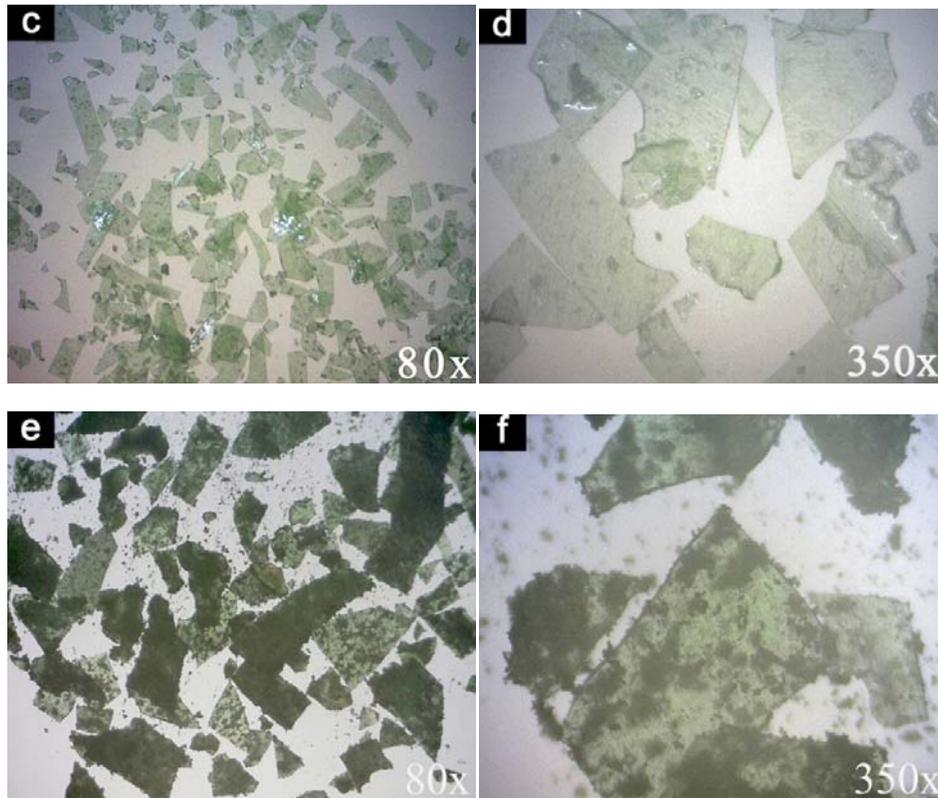


Figure-4. Optical images of Ni(OH)₂ films deposited under different current densities and separated from electrode: (a, b) at 0.313 mA/cm², (c, d) 2.5 mA/cm², (e, f) 5 mA/cm².

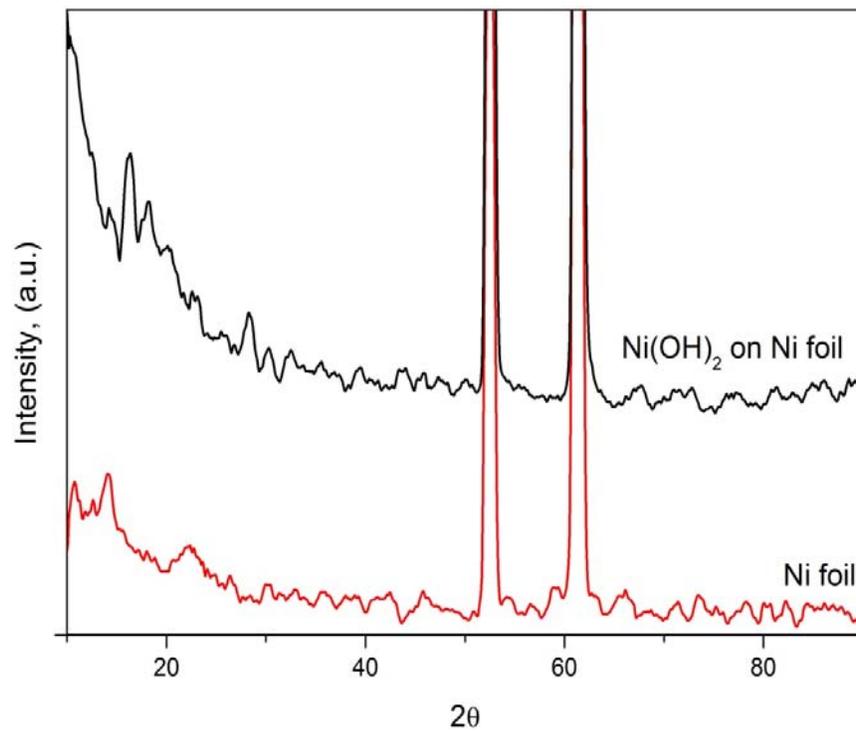


Figure-5. XRD patterns of nickel hydroxide film with substrate electroplated at 0.625 mA/cm² from electrolyte with 5% PVA and electrochemically polished nickel substrate.

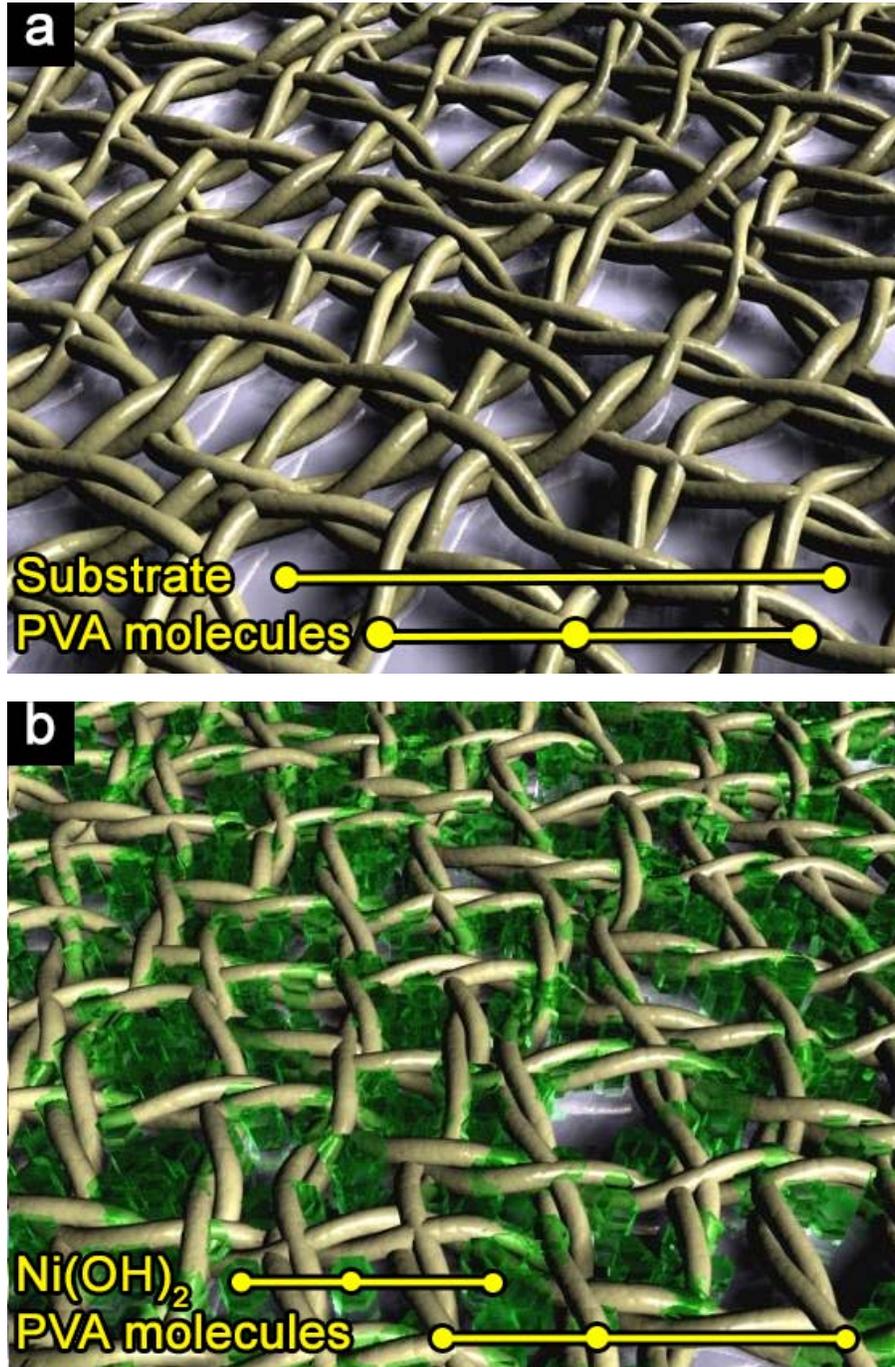


Figure-6. Visualization of the mechanism of electrochemical template synthesis of Ni(OH)₂/PVA film: a - 3D network of PVA (as a template) on the substrate surface; b - composite film, consists of PVA matrix and nickel hydroxide particles as electrochromic. (gray fibers - PVA, green crystals - Ni(OH)₂)

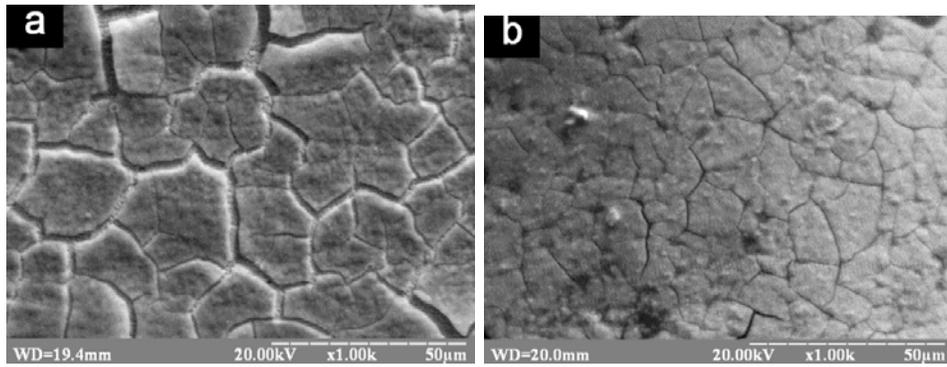


Figure-7. SEM Images of $\text{Ni}(\text{OH})_2$ films deposited at 1.25 (a) and 0.625 (b) mA/cm^2 onto the nickel substrate by template synthesis.

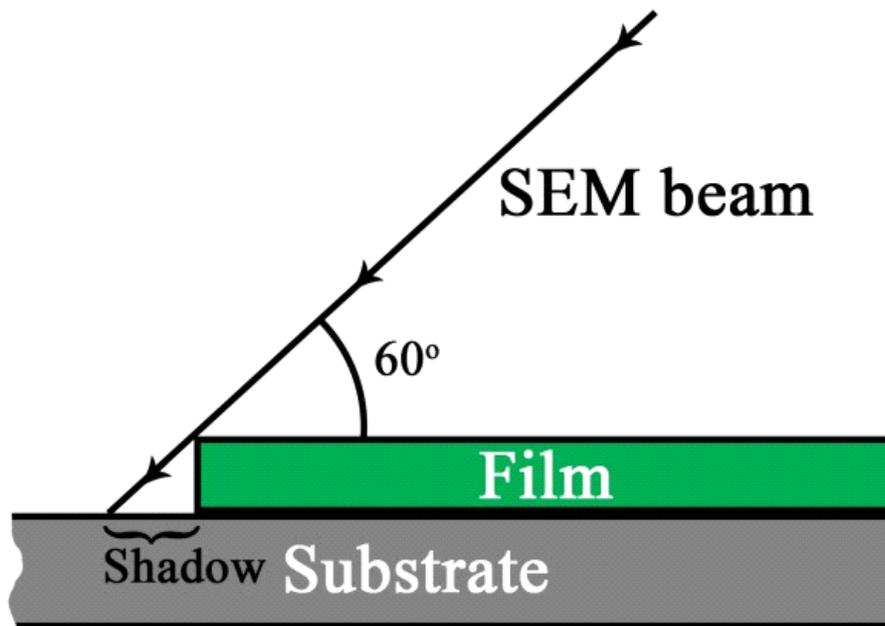


Figure-8. Dropping shadow scheme of the nickel substrate.

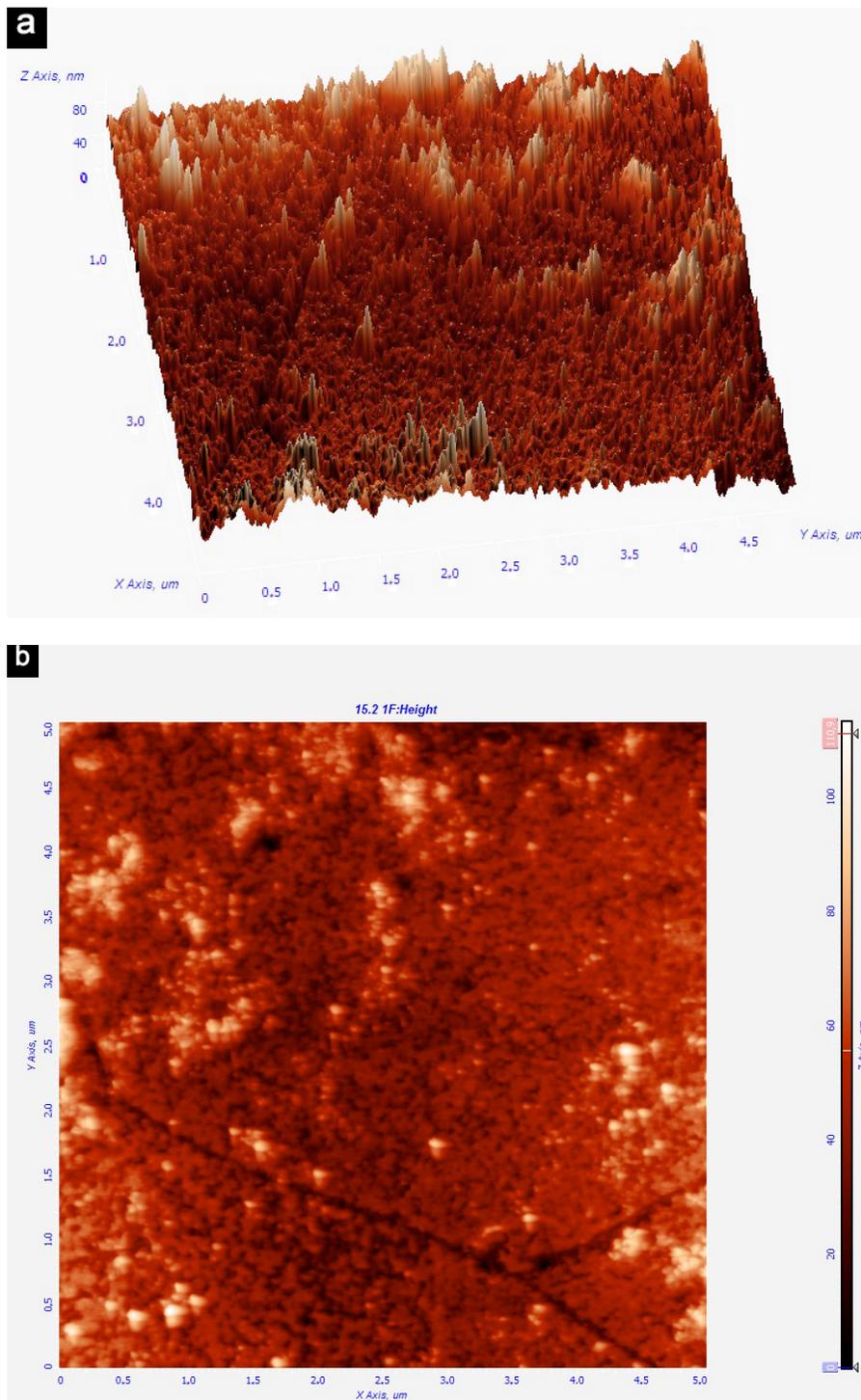


Figure-9. AFM images of Ni(OH)₂ film deposited at and 0.625 mA/cm² onto the nickel substrate by template synthesis.

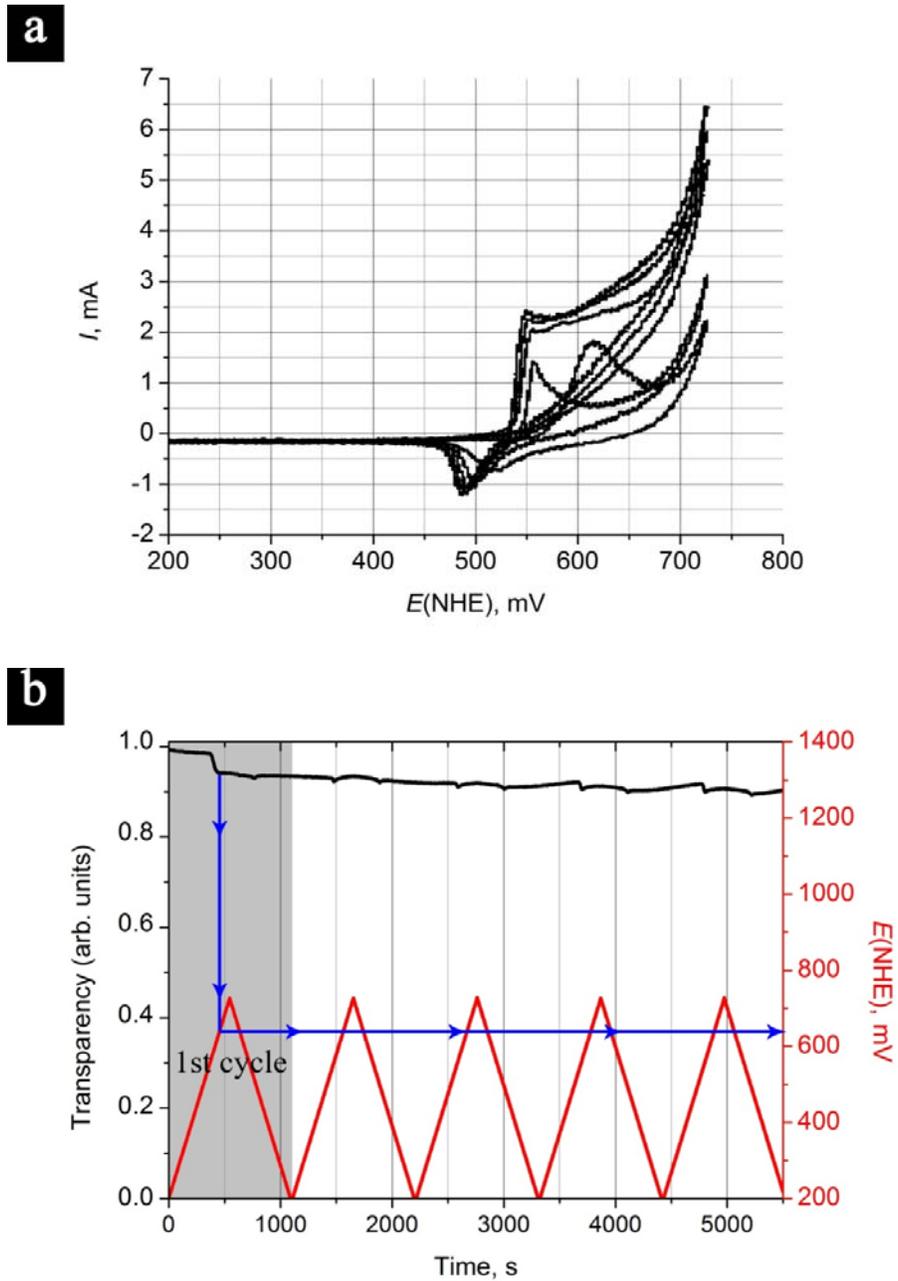


Figure-10. (a) Cyclic voltammetry and (b) colorization curve of the nickel substrate without electrochromic deposited film. The blue line is just to guide the eyes and to indicate the potential at which the color change occurs, i.e. xxx mV.

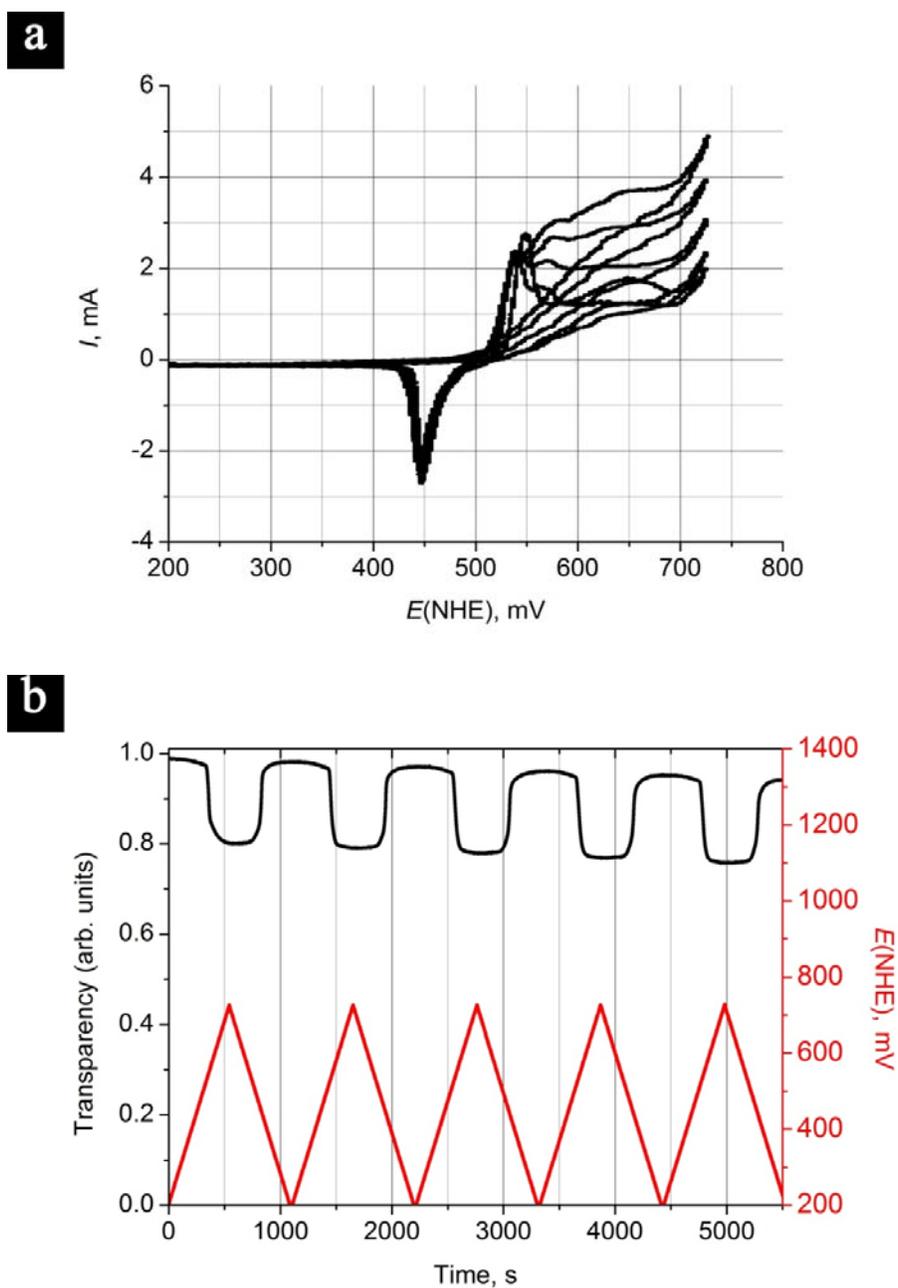


Figure-11. (a). cyclic voltammety and (b) colorization curve of electrode with electrochromic film, deposited by template synthesis and dried at 90°C.

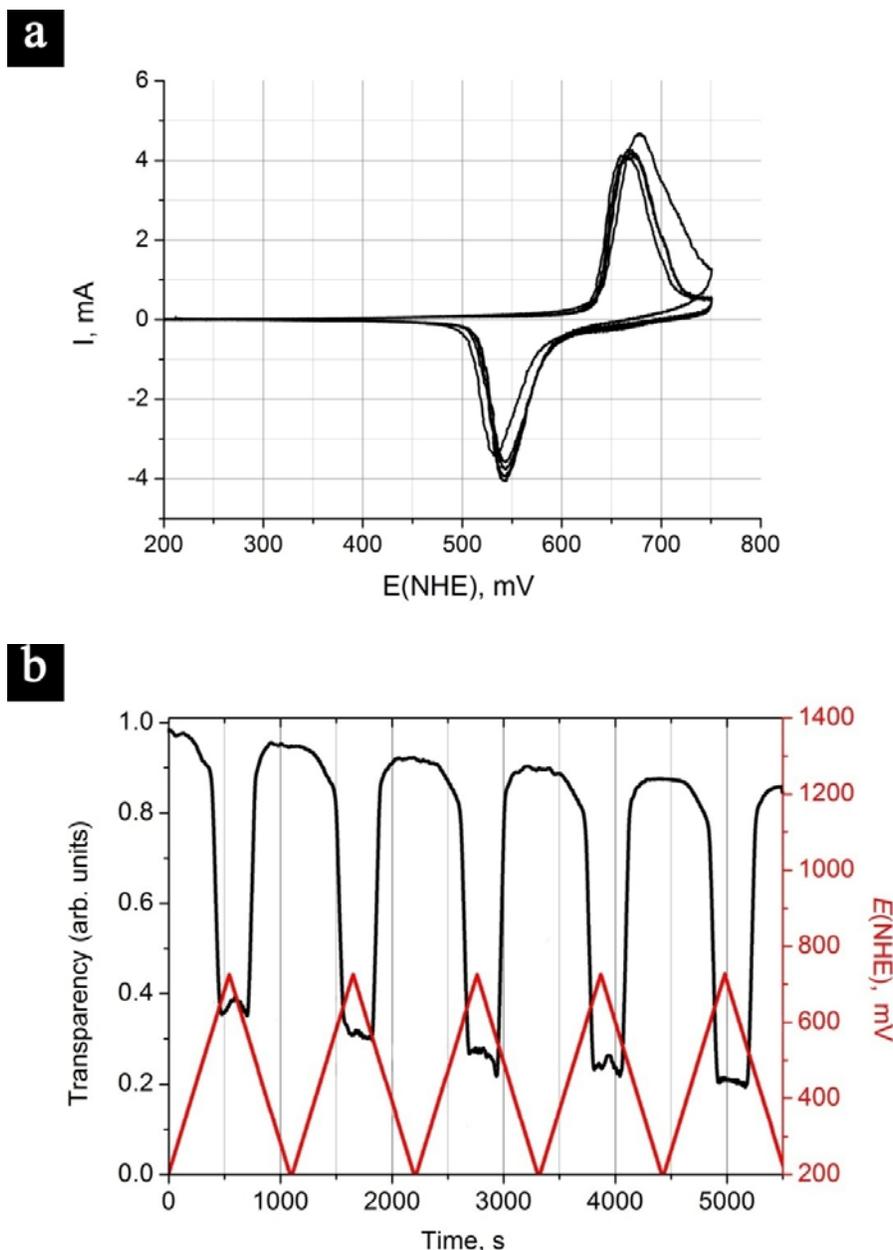


Figure-12. (a). cyclic voltammetry curve and (b) colorization curve of electrode with electrochromic film deposited by template synthesis and dried at 20°C.

Table-1. Elementary analysis according to EDX for nickel hydroxide film with substrate electroplated at 0.625 mA/cm² from electrolyte with 5% PVA

Element	Weight %	Weight % Error	Atom %	Atom % Error
C	9.57	+/- 0.43	31.55	+/- 1.43
O	4.14	+/- 0.19	10.25	+/- 0.48
Co	0.14	+/- 0.22	0.09	+/- 0.15
Ni	86.15	+/- 1.23	58.11	+/- 0.83
Total	100.00		100.00	



4. CONCLUSIONS

It has been shown that the pure Ni(OH)₂ films obtained by electrochemical deposition after drying exhibits , cracks and demonstrating very weak adhesion to the substrate. This outcome confirms all the data previously reported in the literature. On the contrary, it is demonstrated the use of PVA template electrochemical synthesis yields nickel hydroxide/PVA composite films having high plasticity, effective adhesion to substrate and good optical and electrochemical properties. The optimization of advanced Ni(OH)₂/PVA composite films deposition, has been carried out. The influence of the deposition current density on structure, surface morphology and transparency of pure Ni(OH)₂ film has been investigated first. It has been established that optimal current density of 0.625 mA/cm² was the best compromise for obtaining a film with good transparency while maintaining the deposition time short enough, i.e. 80 min. for a 5.16 μm thick film. Overall, the films deposited with PVA template method exhibit an amorphous X-ray structure which can be assumed to arise from the Ni(OH)₂ particle constrained growth in the nano-size cells of the 3D network of the template. The optimal concentration of PVA was determined to be 5% wt. in the deposition solution. The rate of electrode position by template synthesis in the presence of PVA was estimated to be about 3.87 μm/h at the current density of the 0.625 mA/cm² in accordance with the data reported elsewhere. It was also observed by EDX analysis, that PVA is well incorporated inside the nickel hydroxide film. By means of a electrochemical/optical coupled experiment it has been established that the presence of PVA had no negative effect on electrochemical (charge/discharge) activity and optical (coloring/bleaching) reversibility. The electrochromic properties of the composite PVA/Ni(OH)₂ films, deposited by electrochemical template synthesis and dried at 20 °C and 90 °C were also investigated. It has been shown that both temperature treatments yield films with good properties (charge/discharge and colorization-bleaching processes). However, it can be noted that films, dried at 20°C, exhibit the better electrochemical properties and higher colorization degree, while the reversibility of the colorization/bleaching process is better for the sample dried at 90 °C.

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REFERENCES

- [1] Niklasson G.A., Granqvist C.G. 2007. Electrochromics for smart windows: thin films of tungsten oxide and nickel oxide, and devices based on these. *J. Mater. Chem.* 17: 127-156.
- [2] Wang J., Sun X.W., Jiao Z. 2010. Application of Nanostructures in Electrochromic Materials and Devices: Recent Progress. *Materials*. 3: 5029-5053.
- [3] Gillaspie D.T., Tenent R.C., Dillon A.C. 2010. Metal-oxide films for electrochromic applications: present technology and future directions. *J. Mater. Chem.* 20: 9585-9592.
- [4] Tajima K., Hotta H., Yamada Y., Okada M., Yoshimura K. 2011. Surface Analysis of Electrochromic Switchable Mirror Glass Based on Magnesium-Nickel Thin Film in Accelerated Degradation Test. *Materials Transactions*. 52: 464-468.
- [5] Pawlicka A. 2009. Development of Electrochromic Devices. *Recent Pat. Nanotechnol.* 3: 177-181.
- [6] Masaya C., Ishikawa M. 1994. Enhanced Electrochromic Property of Nickel Hydroxide Thin Films Prepared by Anodic Deposition. *J. Electrochem. Soc.* 141: 3439-3443.
- [7] Monk P.M.S., Ayub S. 1997. Solid-state properties of thin film electrochromic cobalt-nickel oxide, *Solid State Ionics*. 99: 115 -124.
- [8] Monk P.M.S., Mortimer R.J., Rosseinsky D.R. 1984. *Electrochromism: Fundamentals and Applications*, VCH, Weinheim, New York, Basel, Cambridge, Tokyo.
- [9] Monk P.M.S., Mortimer R.J., Rosseinsky D.R. 2007. *Electrochromism and electrochromic devices*, Cambridge University Press, The Edinburgh Building, Cambridge, UK.
- [10] Gomathi H., Jayalakshmi M., Joseph J., Vittal R. 2003. Electrochemistry in electrochromism-manifestation by transition metal oxides. *Bull. Electrochem.* 19: 09-16.
- [11] Kadam L.D., Pawar S.H., Patil P.S. 2001. Studies on ionic intercalation properties of cobalt oxide thin films prepared by spray pyrolysis technique. *Mater. Chem. Phys.* 68: 280-282.
- [12] Sharma P.K., Fantini M.C.A., Gorenstein A. 1998. Synthesis, characterization and electrochromic properties of Ni_xOH_y thin film prepared by a sol-gel method. *Solid State Ionics*. 113-115: 457-463.



- [13] Svensson J.S.E.M., Granqvist C.G. 1987. Electrochromism of nickel-based sputtered coatings. *Sol. Energy Mater.* 16: 19-26.
- [14] Svensson J.S.E.M., Granqvist C.G. 1986. Electrochromic hydrated nickel oxide coatings for energy efficient windows: Optical properties and coloration mechanism. *Appl. Phys. Lett.* 49: 1566-1568.
- [15] Ahn K.S., Nah Y.C., Sung Y.E. 2002. Surface morphological, microstructural, and electrochromic properties of short-range ordered and crystalline nickel oxide thin films. *Appl. Surf. Sci.* 199: 259-269.
- [16] Vidotti M., Cyrdoba de Torresi S.I. 2009. Electrostatic layer-by-layer and electrophoretic depositions as methods for electrochromic nanoparticle immobilization. *Electrochim. Acta.* 54: 2800-2804.
- [17] Alkahlout A. 2006. Electrochromic properties and coloration mechanisms of sol-gel NiO-TiO₂ layers and devices built with them, Dissertation, Saarbrücken.
- [18] Vaezi M.R., Sadrnezhaad S.K. 2008. Two-stage chemical deposition of oxide films. *Int. J. Eng., Trans. B.* 21: 65.
- [19] Jayashree R.S., Vishnu Kamath P. 1999. Factors governing the electrochemical synthesis of a-nickel (II) hydroxide. *J. Appl. Electrochem.* 29: 449-454.
- [20] Fomanyuk S.S., Krasnov Y.S., Kolbasov G.Y. 2013. Kinetics of electrochromic process in thin films of cathodically deposited nickel hydroxide. *J. Solid State Electrochem.* 17: 2643-2649.
- [21] Streinz C.C., Hartman A.P., Motupally S., Weidner J.W. 1995. The Effect of Current and Nickel Nitrate Concentration on the Deposition of Nickel Hydroxide Films. *J. Electrochem. Soc.* 142: 1084-1089.
- [22] Umeokwonna N.S., Ekpunobi A.J., Ekwo P.I. 2015. Effect of cobalt doping on the optical properties of nickel cobalt oxide nanofilms deposited by electrodeposition method. *International Journal of Technical Research and Applications.* 3(4): 347-351.
- [23] Sonavane A.C., Inamdar A.I., Shinde P.S., Deshmukh H.P., Patil R.S., Patil P.S. 2010. Efficient electrochromic nickel oxide thin films by electrodeposition. *J. Alloys Compd.* 489: 667-673.
- [24] Ragan D.D., Svedlindh P., Granqvist C.G. 1998. Electrochromic Ni oxide films studied by magnetic measurements. *Sol. Energy Mater. Sol. Cells.* 54: 247-254.
- [25] Fantini M., Gorenstein A. 1987. Electrochromic nickel hydroxide films on transparent/conducting substrates. *Sol. Energy Mater.* 16: 487-500.
- [26] Chia-Ching L. 2012. Lithium-driven electrochromic properties of electrodeposited nickel hydroxide electrodes. *Sol. Energy Mater. Sol. Cells.* 99: 26-30.
- [27] Carpenter M.K., Corrigan D.A. 1989. Photoelectrochemistry of nickel hydroxide thin films. *J. Electrochem. Soc.* 136(4): 1022-1026
- [28] Provazi K., Giz M.J., Dall'Antonia L.H., Cordoba de Torresi S.I. 2001. The effect of Cd, Co, and Zn as additives on nickel hydroxide opto-electrochemical behavior. *J. Power Sources.* 102: 224-232.
- [29] Chigane M., Ishikawa M. 1994. Enhanced electrochromic property of nickel hydroxide thin films prepared by anodic deposition. *J. Electrochem. Soc.* 141(12): 3439-3443.
- [30] Natarajan C., Ohkubo S., Nogami G. 1996. Influence of film processing temperature on the electrochromic properties of electrodeposited nickel hydroxide. *Solid State Ionics.* 86-88: 949-953.
- [31] Hall D. S., Lockwood D. J., Bock C., MacDougall B. R. 2015. Nickel hydroxides and related materials: a review of their structures, synthesis and properties. *Proc. R. Soc. A.* 471(2174): 20140792.
- [32] Hall D.S., Lockwood D.J., Poirier S., Bock C., MacDougall B.R. 2012. Raman and Infrared spectroscopy of α and β phases of thin nickel hydroxide films electrochemically formed on nickel. *J. Phys. Chem. A.* 116: 6771-6784.
- [33] Kotok V.A, Koshel N.D., Kovalenko V.L., Malishev V.V. 2007. Nickel hydroxide ageing in different medias and its influence on electrochemical behavior in composition nickel electrode. 8th Advance Batteries and Accumulators, Brno.
- [34] Guerlou-Demourgues L., Denage C., Delmas C. 1994. New manganese-substituted nickel hydroxides: Part 1. Crystal chemistry and physical characterization. *J. Power Sources.* 52: 269-274.



- [35] Rajamathi M., Kamath P. V., Seshadri R. 2000. Polymorphism in nickel hydroxide: role of interstratifications. *J. Mater. Chem.* 10: 503-506.
- [36] Ecsedi Z., Lazău I. and Păcurariu C. 2007. Synthesis of mesoporous alumina using polyvinyl alcohol template as porosity control additive. *Process. Appl. Ceram.* 1(1-2): 5-9.
- [37] Pon-On W., Meejoo S., Tang I.-M. 2008. Formation of hydroxyapatite crystallites using organic template of polyvinyl alcohol (PVA) and sodium dodecyl sulfate (SDS). *Mater. Chem. Phys.* 112(2): 453-460.
- [38] Miyake K., Hirota Y., Uchida Y. *et al.* 2016. Synthesis of mesoporous MFI zeolite using PVA as a secondary template. *J. Porous Mater.* 23(5): 1395-1399.
- [39] Wanchanthuek R., Thapol A. 2011. The Kinetic Study of Methylene Blue Adsorption over MgO from PVA Template Preparation. *Journal of Environmental Science and Technology.* 4: 552-559.
- [40] Parkhomchuk E. V., Sashkina K. A., Rudina N. A., Kulikovskaya N. A., Parmon V. N. 2013. Template synthesis of 3D-structured macroporous oxides and hierarchical zeolites. *Catal. Ind.* 5(1): 80-89.
- [41] Tan Y., Srinivasan S., and Choi K.-S. 2005. Electrochemical Deposition of Mesoporous Nickel Hydroxide Films from Dilute Surfactant Solutions. *J. Am. Chem. Soc.* 127: 3596-3604.
- [42] Kabita B., Mausumi D., Deepali S. 2015. Polypyrrole Nanonetwork Embedded in Polyvinyl Alcohol as Ammonia Gas Sensor. *Res. J. Chem. Sci.* 5(5): 61-68.
- [43] Gu W., Liao L.S., Cai S.D., Zhou D.Y., Jin Z.M., Shi X.B., Lei Y.L. 2012. Adhesive modification of indium-tin-oxide surface for template attachment for deposition of highly ordered nanostructure arrays. *Appl. Surf. Sci.* 258: 8139-8145.
- [44] Kotok V.A., Kovalenko V.L., Ananchenko B.A., Levko E.N. 2014. The deposition of electrochromic film based on nickel hydroxide by electrochemical method. XV International scientific conference «New Technologies and achievements in metallurgy, materials engineering and production engineering», Materials Engineering, Czestochowa, Poland, Collective Monografie.
- [45] Kotok V.A., Malahova E.V., Kovalenko V.L., Baramzin M.N., Kovalenko P.V. 2016. Smart windows: cation internal and anion external activation for electrochromic films of nickel hydroxide. *Promising Materials and Processes in Technical Electrochemistry, Monograph, KNUTD, Kyiv.*