

STUDY OF THE Ni(OH)₂ ELECTROCHROMIC PROPERTIES OF FILMS DEPOSITED ON FTO GLASS WITH AN ADDITIONAL CONDUCTING LAYER

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Abstract

This work attempts to evaluate the influence of substrate conductivity on electrochromic and electrochemical properties of Ni(OH)₂/PVA composite films, including coloration and bleaching rate. The conductivity of FTO glass was improved by depositing

a silver grid with differing line densities. For deposition of the silver lines, aerosol jet printing method was used. As a result, few electrochromic films were deposited onto bare FTO glass and FTO glass with silver grid deposited onto it. In order to investigate deposited electrochromic films, the cyclic voltammetry with simultaneous recording of the optical characteristics is used. The optical characteristics of films were rather close to each other. At the same time, their electrochemical properties are different. It is found that the additional peaks observed is that of silver, which is electrochemically active in used potential window. In addition it was observed that during electrochemical cycling of $\text{Ni(OH)}_2/\text{PVA}$ deposited on substrates with silver grid, the last changed color from shiny metallic to black color. It is proposed that color changes of silver grid caused by silver transforming to Ag_2O or AgO and back to metallic silver. It is found, that for small areas of electrochromic platings, substrate resistivity has a negligible effect on coloration and bleaching rates. The coloration and bleaching rates for $\text{Ni(OH)}_2/\text{PVA}$ films deposited onto the bare substrate, the substrate with a silver grid (1 cm cell size) and the substrate with a silver grid (0.5 cm cell size) were: -1.45 , -1.71 , -1.40 and 1.1 , 0.75 , 0.84 $\% \cdot \text{s}^{-1}$. It is suggested that the effect of substrate conductivity will clearly be seen when the physical sizes of substrate increase. Also it was underlined that for further experiments for effect definition of substrate resistivity on electrochromic properties inherit conductive materials should be used.

Keywords: Ni(OH)_2 , nickel hydroxide, polyvinyl alcohol, conductive coat, silver, conductivity.

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1. Introduction

«Smart» windows are devices that allow for control over passing light flux by changing their optical parameters [1]. These devices can have a wide range of applications: interior design, adjustable shaded windows for cars and planes, curtains for examination and meeting rooms, etc. Nevertheless, the most important application is the industrial glazing of modern buildings [2]. The use of “smart” windows can lead to significant power savings (up 49 %) on air conditioning. The use of these devices would also lower power consumption during peak periods (morning, evening), and decrease lighting costs [3]. “Smart” windows can be made with electrochrome as an active element, which can be based on different systems. Liquid crystals, suspended particles, electrochemical electrochromic material can be used to construct electrochromic elements with adjustable parameters [4]. In turn, electrochemical material has a number of advantages over other systems. Electrochemical electrochromic materials consume energy only during switching [5]. The other system requires a constant supply of electrical current to sustain one of the optical states. Additionally, electrochromic materials can have different colors when switched to a color state [6].

One of the electrochromic materials with potential for application in electrochromic devices is Ni(OH)_2 [11, 12]. Papers [13, 14], and also [15, 16] present main problems that were investigated toward a study on this material as an electrochromic film. To utilize optical switching of this material, it is deposited onto the surface of glass or transparent plastic with transpired conductive oxide (TCO) layer. TCO is usually a mixture of oxides which are necessary to supply/collect current for electrochemical reaction to occur. The most commonly used TCO:FTO, ITO, AZO [17, 18]. These materials are semiconductors, which have higher specific resistivity in comparison to the metallic conductor. Depending on composition, thickness and deposition method, TCO can have sheet resistance from thousands to few Ohm/\square .

It can be assumed, that sheet resistance of TCO could impact the performance of electrochromic films (including Ni(OH)_2). However, it exists a lack of information concerning the impact of TCO resistance on the materials' electrochromic properties. Only a few sources can be found [7–9]. In these sources, the non-uniform distribution of current density across the surface is described briefly. The use of low-conductive substrates coupled with relatively large glazing areas leads to using long switching time between colored states in order to decrease a gradient effect that can be clearly seen [10]. In the case of switching time minimization, it has to be used larger current densities. Nevertheless, current densities increasing can lead to a more expressed color gradient effect during changes in optical states. In addition, further increasing current density will lead to switching electrochromic reactions in films towards unwanted reactions. As an example, it can be the electrochemical decomposition of the solvent. In work [9], researches faced non-uniform distribution during a reversible metallic deposition

in a mirror-to-transparent electrochromic device. In order to increase conductivity of a large area prototype, it was used additional Pt-based layer on the top of the ITO glass. It should be noted that the authors of the study also consider Pt nanoparticles as growing sites for the metallic layer.

At the same time, it should be noted that for electrochemical deposition of $\text{Ni}(\text{OH})_2$, specific conductivity of TCO can critically impact the uniformity of resulting film [7] as well. In both described cases (during electrochemical deposition and work) electrochromic performance defined by surface conductivity of TCO.

Following the previous discussion, it was decided to set up the research task as follows – to determine the influence substrate conductivity on electrochemical and electrochromic properties of nickel (II) hydroxide-polyvinyl alcohol composite plating.

In order to increase TCO conductivity, a silver grid [19] was deposited onto FTO glass. With an eye to perform different conductivity, density of silver lines was different. This prepared substrate was then used to deposited composite electrochromic $\text{Ni}(\text{OH})_2$ -polyvinyl alcohol film, which was subjected to study.

2. Methods used in the study of $\text{Ni}(\text{OH})_2$ films deposited on FTO and FTO/Ag grid substrates

2.1. Materials used in the study of $\text{Ni}(\text{OH})_2$ films deposited on FTO and FTO/Ag grid substrates

FTO glass with $10 \Omega/\square$ sheet resistance (Zhuhai Kaivo Optoelectronic Technology Co., China) was used as substrate material. Glass was cut into 3×2 cm slides with 2×2 cm working area.

The initial glass was modified by depositing silver grid onto the conductive layer. Grid was deposited with 5 mm gaps.

The deposition schematic is shown in Fig. 1. A jet device was loaded with ink containing silver nanoparticles and was fed with pressurized argon, which sprays silver onto the heated glass. Few samples of FTO glass with silver grid were prepared.

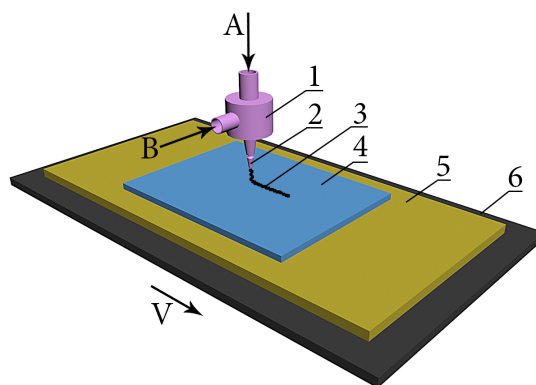


Fig. 1. Schematic of experimental setup forming conductive silver lines on heated substrate:

A – flow of silver particle aerosol; B – carrier flow; V – velocity of substrate movement;
1 – jet device; 2 – nozzle; 3 – printed line; 4 – heated FTO glass; 5 – heating element;
6 – mobile base

After the deposition of the silver grid, the electrochromic film was deposited on modified and unmodified substrates.

Before the deposition of nickel hydroxide film, the surface of substrates was thoroughly cleaned and degreased. The first stage was washing with a soda solution and distilled water. Next stage – degreasing with ethanol and drying. Cathodic template deposition was conducted using electrolyzer shown in Fig. 2.

Deposition parameters: cathodic current density $0.1 \text{ mA}/\text{cm}^2$, deposition time 10 min. After deposition, electrodes were drying on air for an hour.

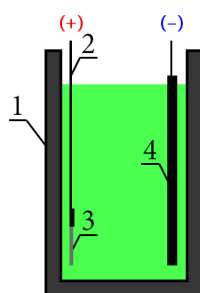


Fig. 2. Schematic of electrolyzer for film deposition: 1 – PMMA frame; 2 – cathode current lead; 3 – cathode FTO glass with/without Ag grid; 4 – anode (nickel foil); green depicts electrolyte solution: 0.01 M $\text{Ni}(\text{NO}_3)_2$ and 50 g/l polyvinyl alcohol (PVA)

2. 2. Equipment and conditions for the study of $\text{Ni}(\text{OH})_2$ films deposited on FTO and FTO/Ag grid substrates

Electrochemical characteristics were measured using digital potentiostat which was connected as shown in **Fig. 3**. The optical response was recorded simultaneously with electrochemical measurements, using ADC, **Fig. 3**.

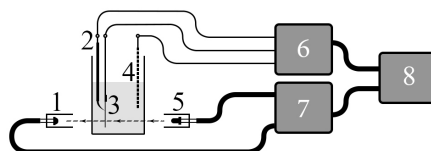


Fig. 3. Schematic of experimental setup for electrochemical and electrochromic tests: 1, 5 – photoresistor and photodiode; 2 – reference electrode; 3 – working electrode (electrode with electrochromic film); 4 – counter-electrode; 6 – digital potentiostat Elins P-8 (Russia); 7 – setup for recording optical characteristics: stabilized current supply, analog-to-digital converter (DAC) E-154 (Russian Federation); 8 – personal computer

0.1 M KOH was used as an electrolyte for all measurements. Potentiodynamic cycling was conducted from +201 to +751 mV vs. NHE at 1 mV/s.

Electrodes were photographed in their color state for visual inspection.

3. Results of studying electrochromic films with an additional conductive layer on a substrate

Fig. 4 shows results for the film deposited on FTO glass without the Ag grid conductive layer. Analysis of cyclic voltammetry (CV) curve allows concluding that oxidation and reduction reactions of the film on such substrate are rather stable, as peak height and position are constant. It should be noted that peak potential is +659 mV anodic, +528 mV cathodic. The difference between peak positions is semi-quantitative criteria of reversibility, and for this sample is equal to 131 mV.

Coloration-bleaching curve (**Fig. 4, b**) characterizes this sample as having good optical properties, which determined by coloration degree good bleaching reversibility, and stable curve shape. The shape of the curve is close to rectangular, which is most optimal for use in electrochromic devices. The coloration degree here means a difference between transparency in colored and bleached states for a given cycle or averaged between a few cycles. In turn, bleaching irreversibility, which for this sample was close to zero, refers to different transparency values in the initial state and on the last coloration-bleaching cycle. Additionally, averaged coloration degree for this sample is 76.5 % (2–4 cycles).

The next sample was deposited onto the substrate with a silver grid (a square with 1 cm edge). The results for this sample are shown in **Fig. 5**. CV curve for this sample is rather atypical. In addition to oxidation and reduction peaks of $\text{Ni}(\text{OH})_2$ (+705, +577 mV), there are also few additional peaks at +340, +375, +510 and +558 mV. Additionally, the shape and size of the additional peak were changing constantly.

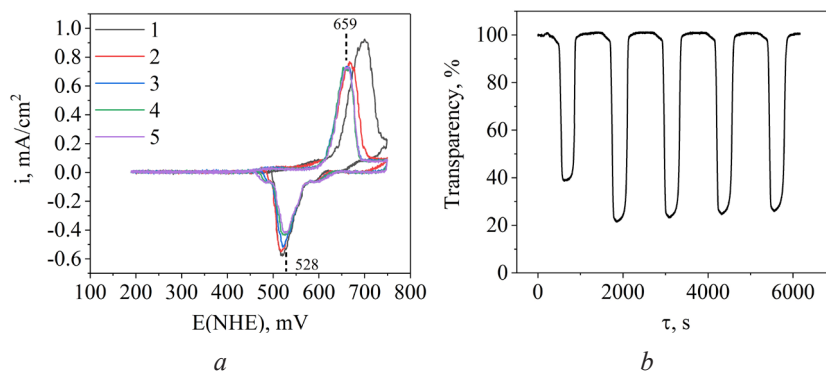


Fig. 4. Characteristic for film deposited onto FTO without silver grid:
a – CV; *b* – coloration bleaching curve

In turn, the coloration bleaching-curve showed somewhat worse results than the previous sample.

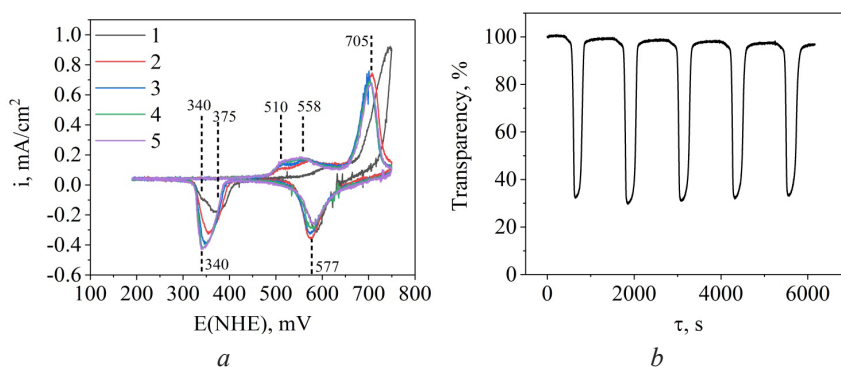


Fig. 5. Characteristics for the film deposited onto FTO with a silver grid (cell size 1 cm):
a – CV; *b* – coloration bleaching curve

Bleaching irreversibility was about 3 %, with a coloration degree from cycles 1–4 – 67 %. Curve shape was close to rectangular only at the part of the coloration start and end of the bleaching process **Fig. 4, b**.

Data for sample deposited onto FTO/Ag grid (0.5 cm edge length) is shown in **Fig. 6**. The cyclic voltammogram curve shows additional peaks, the same as in **Fig. 5**. Additionally, these peaks are more pronounced, than for the grid with a square edge of 1 cm. Oxidation/reduction peaks of nickel hydroxide are also somewhat higher.

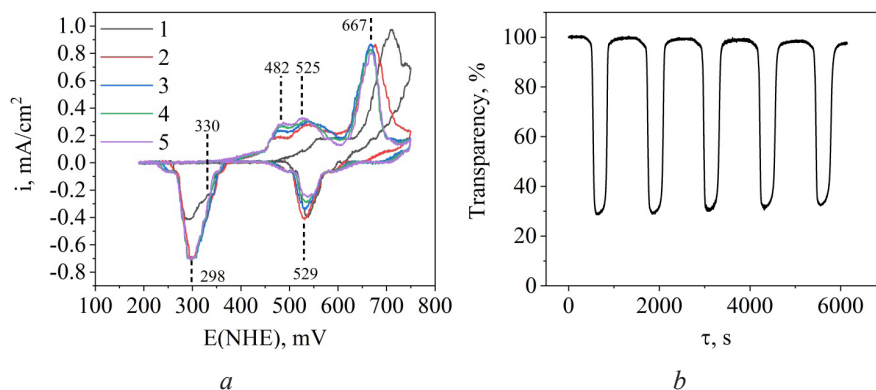
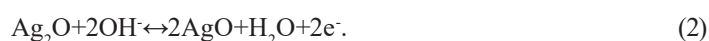


Fig. 6. Characteristics for the film deposited onto FTO with a silver grid (cell size 0.5 cm):
a – CV; *b* – coloration bleaching curve

The optical characteristics of this film are good, as the coloration degree is 68 % (2–4 cycle), and bleaching irreversibility 2 %. Curve shape.

4. Discussion of results from studying the effect of addition conductive layer on electrochromic and electrochemical properties of films

Analysis of the presented CV curve for films deposited on different substrates allows concluding that the silver grid is not passive. It should be noted additional peaks appear in presence of silver deposited onto FTO. The later do increase with the increase of grid line density, which is a proof of assumption regarding the involvement of silver in reaction. It was also observed, that the outer shiny part of silver changed its color to black in the range of positive potentials. This like was caused by reversible electrochemical reactions [20–22]:



Considering that all silver oxides have a dark color, and color change was reversible, reactions (1) and (2) are reversible. This is also evident from CV.

Small potential changes of anodic peak (about +700 mV) and cathodic peak (about +550 mV) potentials, is likely due to a slight difference during the deposition of electrochromic films. The difference lies in the presence of a silver grid and its line density for different substrates. This can affect film deposition due to the difference in substrate resistance or surface effects. It is interesting, that in substrate series no silver → Ag grid 1 cm → Ag grid 0.5 cm cathodic peak of $\text{NiOOH} \rightarrow \text{Ni(OH)}_2$ decreases, while the anodic peak of the opposite process increases. It appears that with the use of a silver grid, reversibility drops somewhat. A possible explanation is the presence of a parallel process that overlaps with the main process resulting in a change of peak values.

The optical characteristics of films deposited on different substrates did not differ much. As such it was decided to study the last coloration-bleaching cycle in detail and evaluate the rate of bleaching and coloration. The last cycle of different films was compiled into a single graph, shown in Fig. 7, a. It's worth to note, that curves are shifted in time relative to each other for better visibility.

Analysis of curves shown on the figure allows concluding that they have similar slopes. This is especially true for the coloration process. As such straight parts were chosen (outlined with dashed lines) to calculate bleaching rates. A comparison of these values reveals that rates are similar (within the same order) and the difference between them does not exceed $\pm 32\%$. This is despite the fact, that specific resistance of Ag is lower by two orders than that of FTO [23, 24]. This can mean that fall small size electrochromic elements, substrate resistance are not of greater importance, and have little effect on coloration/bleaching rates.

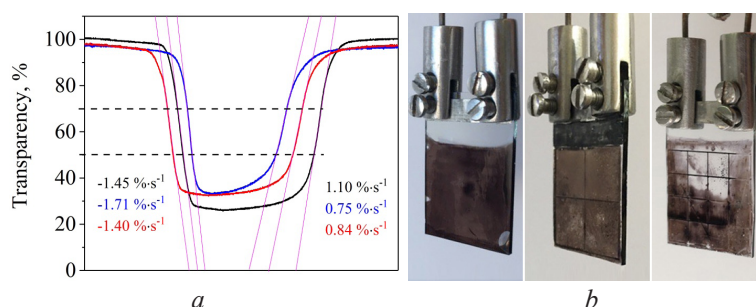


Fig. 7. Results for the obtained samples*: *a* – last cycles of coloration-bleaching curves of films deposited **—** FTO, **—** FTO/Ag grid (1 cm cell), **—** FTO/Ag grid (0.5 cm cell); *b* – photographs of electrodes after cycling; * – the violet color shows tangents of linear parts of the curves; text in black, blue, red – coloration (negative) and bleaching rate correspond to curve color in % per second; dashed lines outline a section of curves that were used to calculate coloration (bleaching) rates

In order to seem the effect of substrate resistance, further studies should be conducted on larger electrode areas. Considering the electrochemical activity of silver, a material that is inert in the electrochrome potential window [+201 mV; +701 mV] has to be used. In addition, photographs of electrodes after shown in **Fig. 7, b**.

5. Conclusions

As a result of conducted work, electrochromic films were deposited onto the different substrates and their electrochromic and electrochemical characteristics were studied. As a consequence of conducted work, the following was found:

- Ag grid deposited onto glass does show electrochemical activity in used potential range, and is reversibly oxidized to oxides. This is due to the presence of anodic peaks at the range [+480; +560] mV and cathodic peaks at the range [+298; +340] mV;
- experiments revealed that for small substrate sizes, the rate of color change does not depend on substrate resistance and it lies in the range from -1.40 to -1.71 %·s⁻¹ for the colorization process. For the bleaching process, the rate lies in the range from 0.75 to 1.1 %·s⁻¹.

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