



OPTIMIZATION OF ELECTROLYTE COMPOSITION FOR THE CATHODIC TEMPLATE DEPOSITION OF Ni(OH)₂-BASED ELECTROCHROMIC FILMS ON FTO GLASS

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ABSTRACT

A series of experiments have been conducted in order to determine the optimal concentration of polyvinyl alcohol (PVA) for deposition of electrochromic nickel hydroxide films onto fluorine-doped tin oxide (FTO), using cathodic template deposition method. Fundamental physicochemical properties of electrolytes for cathodic template deposition method with different concentration of PVA have been studied. It was found that higher concentrations of PVA resulted in higher adhesion of films to FTO substrate and higher performance; however, excessive concentrations resulted in degradation of film performance. It was also found, the electrolyte viscosity is directly dependant on PVA concentration, however, no correlation between PVA concentration and conductivity have been found. A hypothesis was proposed to explain such behavior.

Keywords: electrochromism, nickel hydroxide, polyvinyl alcohol, concentration, template synthesis, viscosity, density, conductivity.

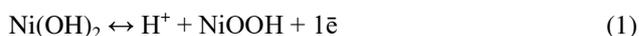
1. INTRODUCTION

The so-called "Smart cities", built of "Smart houses", are the paradigm of the modern development of future energy-independent society. "Smart windows" are one type of "smart electronic" which can be used in "smart" and regular housing. These devices can solve many problems: energy saving, reducing power grid load in "peak" time, improving comfort, automation of the housing process etc. [1, 2]. The active component of such window is an electrochromic component which is can be controlled by a signal to change its optical properties: color, transparency, glossiness, reflection coefficient. Despite electrochromism being known for quite a while, the pilot samples of such windows that are suitable for the mass application have only appeared recently [3]. The ability to control optical characteristics of smart windows enables their use for billboards, manipulation and meeting rooms, interior design, car windows, as displays for a number with slow dynamics (temperature, presser, prices) etc.

Among possible electrochromic systems, few major types can be outlined: liquid crystal (LC) systems, suspended particles (SP) systems, electrochemical systems. LC and SP systems have fast switched between optical states and relatively simple construction, but they require a constant supply of electrical current to sustain switched state and have a high cost. While electrochemical systems have lower switching speeds (second to tens of seconds) and more complex construction, they are

significantly cheaper and do not require constant current supply to sustain the switched state [4].

One of the promising electrochromic materials for smart windows is nickel hydroxide. Its high specific characteristics and high reversibility have proven it as an excellent material for electrical batteries [5-7]. Ni(OH)₂. A thin film of nickel hydroxide is transparent and undergoes drastic color change upon oxidation at anodic potentials [8-10]:



However, low adhesion to transparent conductive substrates [11, 12] and degradation of its electrochromic properties [8, 13, 14] does not allow the full realization of its potential.

Various methods can be used for preparation of nickel hydroxide for electrochromic applications: chemical precipitation [15, 16], homogeneous precipitation [17], dip-coating [18], sol-gel [19-22], reactive magnetron sputtering [23, 24], electrochemical deposition (anodic [25], cathodic [26]), cathodic template deposition [9, 11, 27-32]) can be used for deposition of thin transparent films of Ni(OH)₂. The electrochemical methods have an advantage over ones, as required equipment is relatively cheap and the process can be easily automated for mass production.

Cathodic template method for preparation of Ni(OH)₂ with polyvinyl alcohol (PVA) as a template,



produces uniform films with high adhesion to the substrate [32]. Paper [11] describes optimal PVA template concentration for film deposition onto a metallic substrate. It was found that for 1M nickel nitrate catholyte (anolyte 1M KNO_3 [11]) and cathodic current density of 0.625 mA/cm^2 the optimal PVA concentration is 5 wt%. For film deposition on conductive transparent oxide substrates (ITO and FTO), it was decided to employ one electrolyte (single compartment cell), containing $0.01 \text{ M Ni(NO}_3)_2$. PVA concentration was the same as for metal substrate - 5%. Deposition current density had been decreased to 0.1 mA/cm^2 , and the deposition time was decreased from 80 to 10 minutes. Lower electrolyte concentration and current density were necessary to improve the distribution of current density on the substrate, owing to the significantly lower conductivity of oxide substrates [9]. Because disposition conditions for ITO and FTO were drastically changed, the used PVA concentration could have been suboptimal.

Present work describes a study on optimal PVA concentration and its influence on physicochemical properties of electrolyte (conductivity, viscosity, and density). Because properties of deposition electrolyte can significantly affect the rate and mechanism of deposition reactions, which in turn affect optical characteristics of resulting films, the optimization of electrolyte composition becomes an important problem.

2. MATERIALS AND METHODS

2.1 Reagents and materials used in experiments

Analytical grade reagents and PVA J-POVAL 24-89 were used for the preparation of all solution.

Glass slides coated with fluorine-doped tin oxide (FTO) ($10 \Omega/\square$), with working area of $20 \times 20 \text{ mm}$ have been used as a substrate.

Deposition conditions for all films are listed in Table-1. Nickel plate was used as the anode.

Table-1. Film deposition and drying conditions.

Electrolyte temperature, °C	Cathodic current density, mA/cm^2	Deposition time, min	Drying time, h	Drying temperature, °C
30	0.1	10	24	22

In order to evaluate the influence of PVA concentration on the properties of the resulting film, a set of electrolytes with different PVA concentrations were

prepared. Electrolyte compositions and labels of samples prepared from them are listed in Table-2

Table-2. Electrolyte compositions used for the preparation of Ni(OH)_2 films.

№	1	2	3	4	5	6	7
Electrolyte composition	$0.01 \text{ M Ni(NO}_3)_2 + 5 \text{ g/l PVA}$	$0.01 \text{ M Ni(NO}_3)_2 + 10 \text{ g/l PVA}$	$0.01 \text{ M Ni(NO}_3)_2 + 15 \text{ g/l PVA}$	$0.01 \text{ M Ni(NO}_3)_2 + 20 \text{ g/l PVA}$	$0.01 \text{ M Ni(NO}_3)_2 + 30 \text{ g/l PVA}$	$0.01 \text{ M Ni(NO}_3)_2 + 40 \text{ g/l PVA}$	$0.01 \text{ M Ni(NO}_3)_2 + 50 \text{ g/l PVA}$
Film label	5PVA	10PVA	15PVA	20PVA	30PVA	40PVA	50PVA

2.2 Evaluation of electrochemical and electrochromic characteristics of prepared films

Optical and electrochemical characteristics were studied by means of cyclic voltammetry (CV) with simultaneous recording of the coloration-bleaching process, using the specially constructed cell (Figure-1).

Nickel foil was used as counter-electrode, Ag/AgCl (KCl sat.) was used as a reference electrode, electrolyte - 0.1 M KOH . Optical characteristics were recorded at a rate of 3 Hz using analog-to-digital converter E-154 (Russia), and electrochemical measurement was conducted using digital potentiostat-galvanostat Ellins P-8 (Russia).

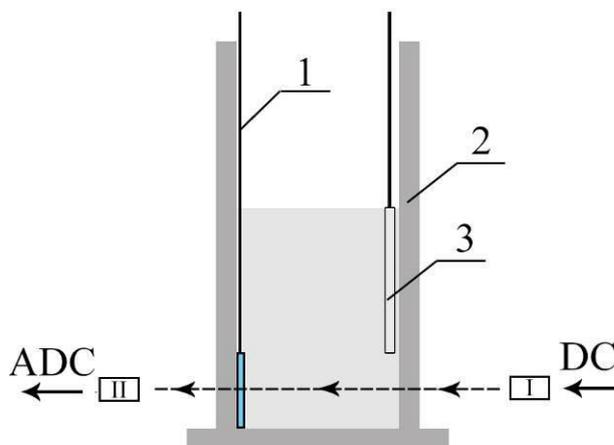


Figure-1. The cell for optical and electrochemical testing of electrode: 1 - Working electrode with film deposition onto FTO glass; 2 - Cell frame made from transparent plastic; 3 - counter electrode; I - the source of whitely light ($5500 \text{ }^\circ\text{K}$); II - photoresistor. DC - the source of stabilized voltage; ADC- analog-to-digital converter



Testing regime: potential window +200 to +725 (+900) mV, scan rate 1 mA/s, number of cycles - 5. Position, size, and shape of peaks on CV curves and differences between cycles were analyzed.

Coloration-bleaching curves were used to derive absolute coloration degree - transparency difference between bleached and colored state on each cycle (Figure-2, values b_1 - b_5). An average coloration degree (D , %) was also calculated for each film according to formula 2:

$$D = \frac{\sum_1^i b_i}{i} \quad (2)$$

where b_i - absolute coloration degree on cycle i (Figure-2),

i - cycle number.

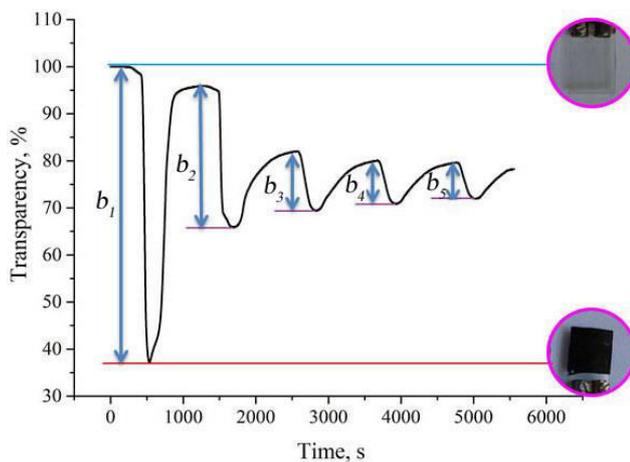


Figure-2. The principle of calculation of absolute coloration degree values from coloration-bleaching curves.

As an additional measure of film quality, an average irreversibility (Z , %) on bleaching were calculated for each film according to formula (3).

$$Z = \frac{\sum_1^i d_i}{i} \quad (3)$$

where d_i - average irreversibility on cycle i (Figure-3),

i - cycle number.

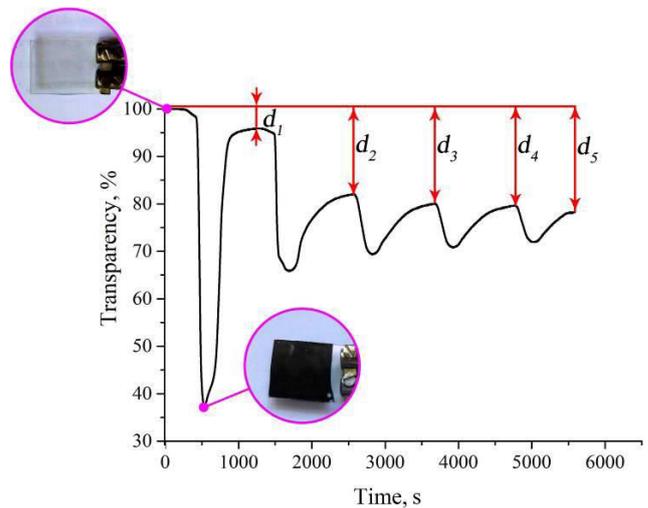


Figure-3. Calculation of irreversibility for films upon bleaching.

2.3 Density measurements

The density of prepared solutions was measured using glass pycnometer with the volume of 10 ml.

Prior to measurements, the pycnometer was thoroughly washed with distilled water and dried in the thermostat. Cold and dry pycnometer was weighted on an analytical scale, filled with studied solution and weighted again. Density was calculated according to the formula:

$$\rho = \frac{m}{V} \quad (4)$$

where m - a mass of the solution, g
 V - pycnometer's volume, cm^3 .

2.4. Viscosity measurements

Viscosity has been studied using rotational viscometer Reologica Instruments StressTech HR.

2.5 Conductivity measurements

The conductivity of the solution was measured using Conductivity Bridge P-5083 and Arrhenius cell using the unplatinized platinum electrodes with a smooth surface, at current frequencies from 50 to 100000 Hz and temperature $25 \pm 0.2^\circ\text{C}$. A batch of each sample solution (25 ml) was previously thermostated before conductometric measurement. The solution in the cell was agitated by means of a magnetic stirrer. The same conditions were also used for measurements using Conductometer with constant frequency (1000 Hz), Mettler Toledo NPC227. In all cases, conductivities of all test solutions were recorded 10 min of equilibration time.

3. RESULTS AND DISCUSSIONS

3.1 Study of optical characteristics

Figure-4a shows results for the film prepared from 0.01 M $\text{Ni}(\text{NO}_3)_2$ with the addition of 5 g/l PVA - sample 5PVA. Analysis of cyclic voltammogram (CV)



allowed drawing few conclusions. Firstly, CV shows well-defined peaks for all cycles, which indicates uniform and fast occurrence of oxidization-reduction reactions in the whole volume of the film. Secondly, the peak current gradually decreases with each cycle, with peak currents of the fifth cycle being 20% of initial values, which indicated degradation of electrochemical characteristics. Coloration-bleaching curve of this film (Figure-5b) shows the rather high initial value of absolute coloration degree of 45%, which rapidly drops to 8%. It should be noted, that film does not return to initial state. Such decrease in characteristics is related to loss of electrical contact of the film with FRO substrate. This conclusion is supported by the visual appearance of the film in colored state Figure-4a. It can be seen that black spots are where the film is still intact with the majority of the electrode being transparent i.e. without the film.

Figure-5 shows results for the film prepared from 0.01 M $\text{Ni}(\text{NO}_3)_2$ with 10 g/l PVA (10PVA) and a photo of the electrode immediately after cycling. Results of this film do not differ much from the previous sample (5PVA). The CV curves show similar behavior in that peak current decrease significantly during cycling and bleaching-coloration curves show degradation of absolute coloration degree. However, the absolute coloration degree and reversibility (Figure-5b) are higher than those of 5PVA. Photo of the electrode (Figure-5a) shows areas where film have had peeled off.

Optical and electrochemical characteristics of sample 15PVA are shown in Figure-6. Oxidation and reduction peak currents (Figure-6a) decrease significantly during cycling, and on 3rd cycle are 10% of the initial values. Similar to the CV curve, the bleach-coloration curve (Figure-6b) shows same degradation: decreases in absolute coloration degree and irreversibility upon bleaching.

The film prepared from solution with PVA concentration of 20 g/l (sample 20PVA) demonstrates significantly better characteristics (Figure-7). CV of this

sample shows the rather good stability of peak current values and their positions. coloration-bleaching curve (Figure-7b) also shows rather good characteristics: the shape is close to rectangular and good reversibility. However, the absolute coloration degree is rather low - 25%, which contrasts with curves of previous samples 5PVA, 10PVA, 15PVA (from 70 to 8% depending on cycle number). Photo of the electrode (Figure-7a) shows that after cycling, the film had remained across the whole working area. This shows, that PVA concentration of 20 g/l is sufficient for formation of $\text{Ni}(\text{OH})_2/\text{PVA}$ composite with good adhesion to substrate.

Figure-8 shows experimental results for the film prepared from electrolyte with 30 g/l PVA (sample 30PVA) and its photo after cycling. In comparison to sample 20PVA, this sample shows a higher absolute coloration degree of 50%. The film also shows deep and uniform coloration (Figure-8a).

The film prepared from electrolyte with PVA concentration of 40 g/l (sample 40PVA) shows the best characteristics in comparison to previous samples: 5PVA, 10PVA, 15PVA, 20PVA, 30PVA. The peak currents on CV are high and are almost independent of cycle number (Figure-9a). It also demonstrates the highest absolute coloration degree that is close to 100% - Figure-9b. Photo image of the electrode after cycling revealed that coloration is deep and very uniform. This allows concluding, that film prepared in presence of 40 g/l PVA posses the best characteristics of analyzed samples.

It was proposed to conduct an additional experiment with PVA concentration of 50 g/l. Results for this film (PVA50) are presented in Figure-10. By analyzing the obtained results, it can be noted that prepared films have good characteristics similar to that repaired at PVA concentration of 40 g/l. However, its absolute coloration degree is lower by $\approx 5\%$. Thus, it can be concluded, that for 0.01 M nickel nitrate electrolyte, the optimal concentration of PVA template is 40 g/l.

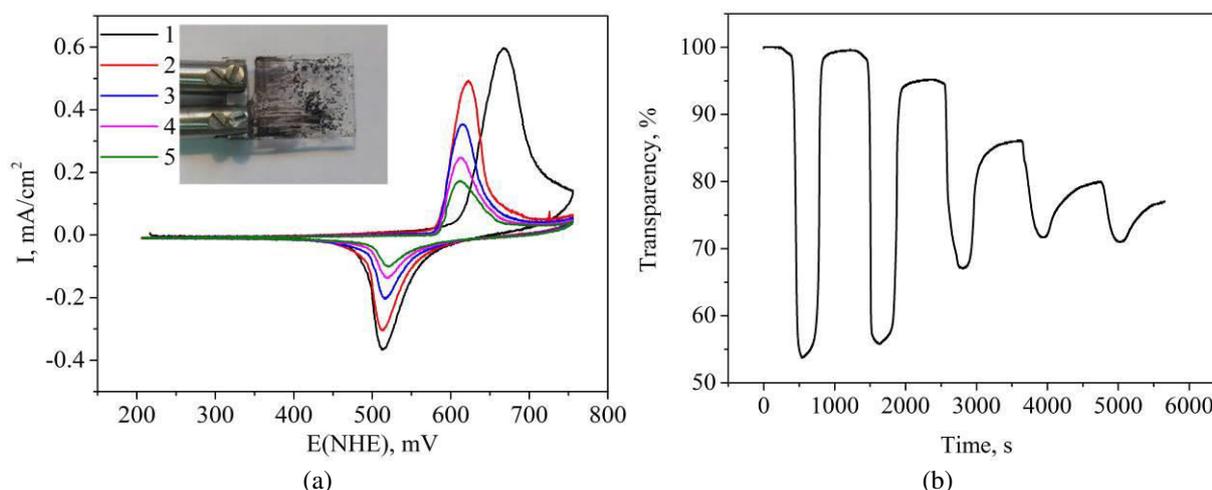


Figure-4. Cyclic voltammogram with a photograph of the colored electrode after cycling (a) and coloration-bleaching curve (b) of film 5PVA

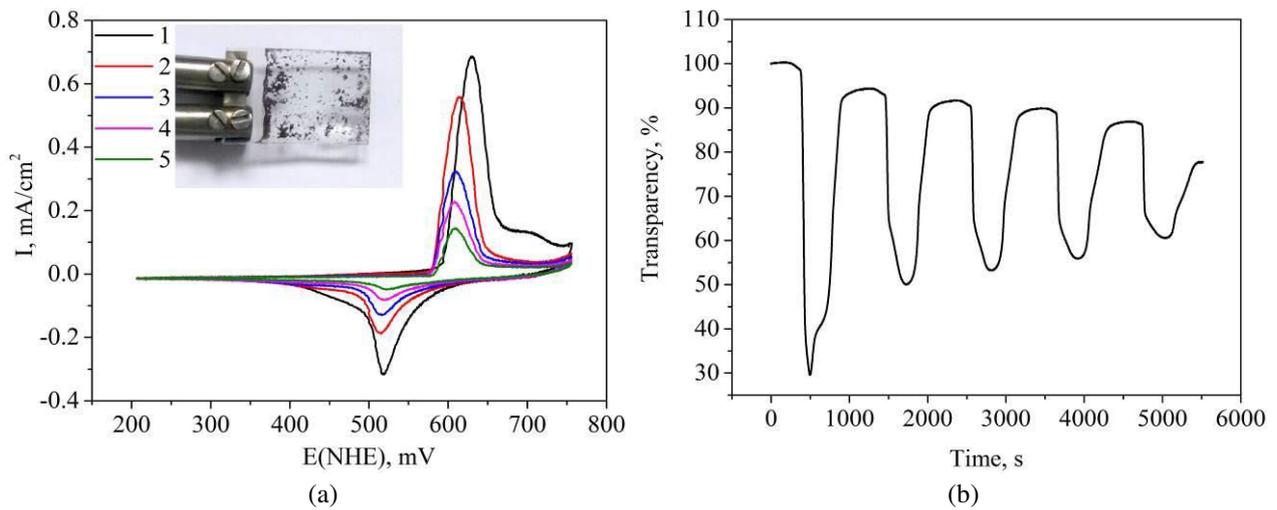


Figure-5. Cyclic voltammogram with a photograph of the colored electrode after cycling (a) and coloration-bleaching curve 10PVA

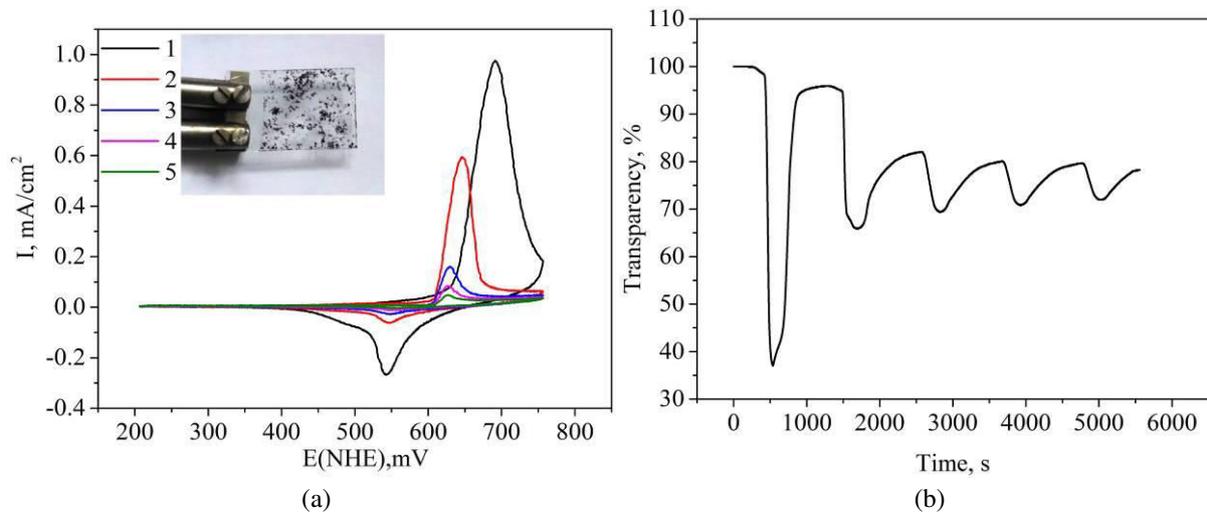


Figure-6. Cyclic voltammogram with a photograph of the colored electrode after cycling (a) and coloration-bleaching curve 15PVA

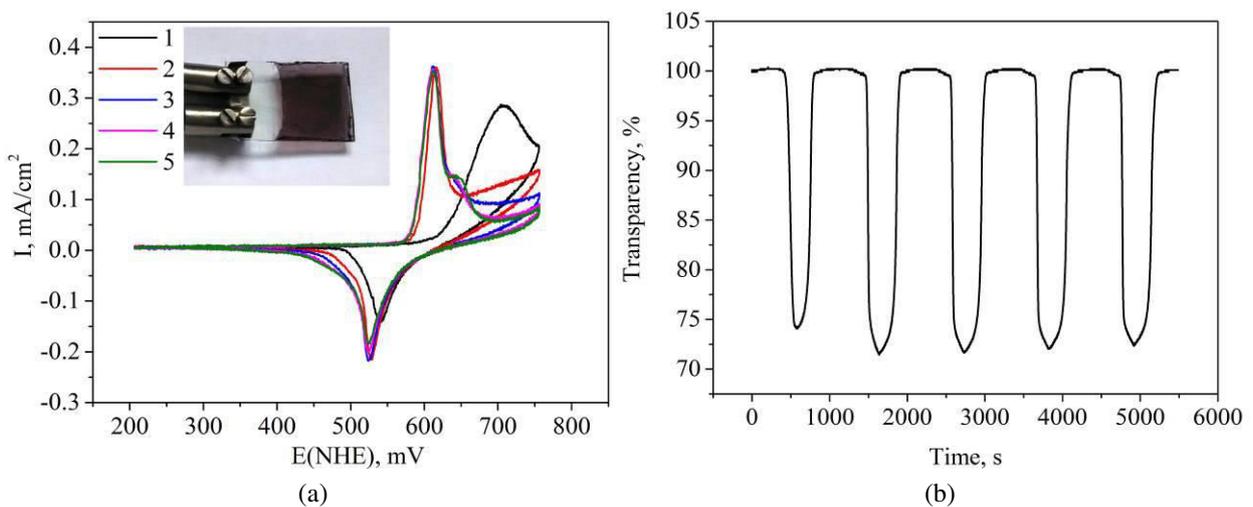


Figure-7. Cyclic voltammogram with a photograph of the colored electrode after cycling (a) and coloration-bleaching curve 20PVA.

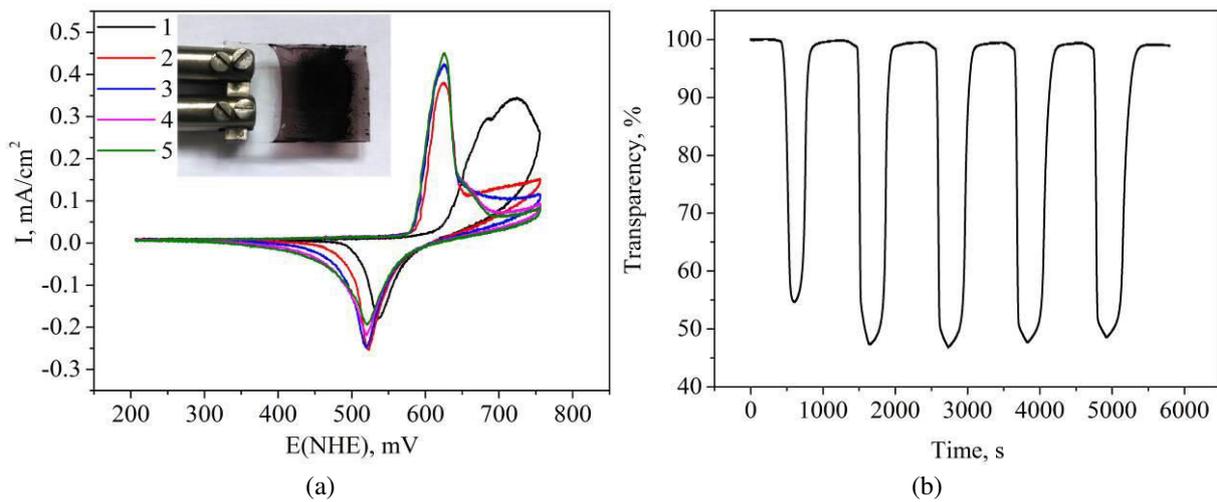


Figure-8. Cyclic voltammogram with a photograph of the colored electrode after cycling (a) and coloration-bleaching curve 30PVA.

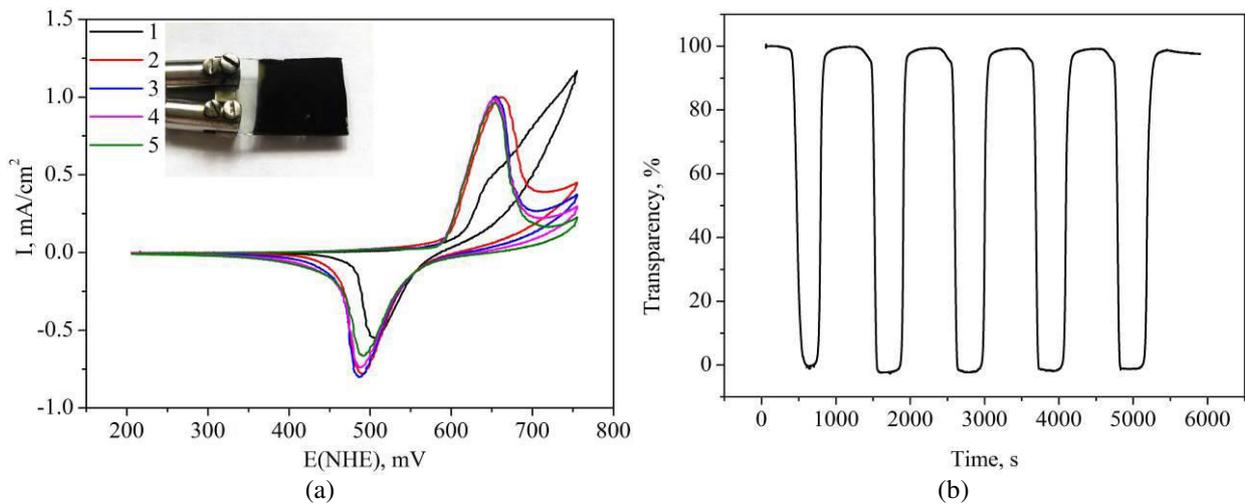


Figure-9. Cyclic voltammogram with a photograph of the colored electrode after cycling (a) and coloration-bleaching curve 40PVA

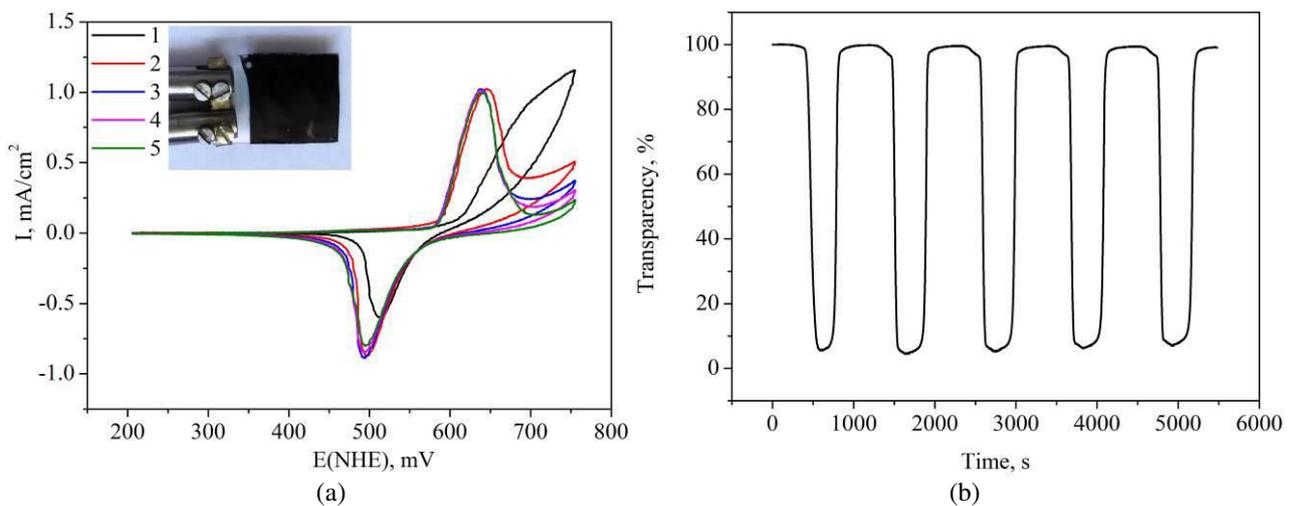


Figure-10. Cyclic voltammogram with a photograph of the colored electrode after cycling (a) and coloration-bleaching curve 50PVA.



An average coloration degree (Figure-11a) and irreversibility upon bleaching (Figure-11b) were calculated for all films. Analysis of Figure-11a allows concluding, that low concentrations of PVA (5 - 20 g/l) in the electrolyte, do not have a significant effect on absolute coloration degree. Starting at 30 g/l the absolute coloration

degree rises significantly. In addition, at a concentration above 20 g/l, the reversibility of the film increases, with an optimum at 40 g/l – Figure-11b. It is worth noting, that the increase of PVA concentration from 40 to 50 g/l. lead to a decrease in absolute coloration degree by 7%.

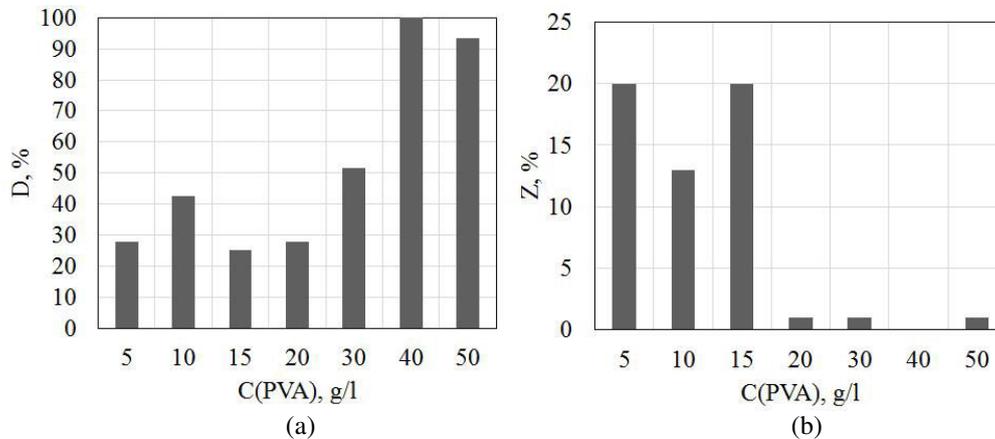


Figure-11. Average coloration degree (a) and irreversibility upon bleaching (b) for films prepared with the different concentration of PVA.

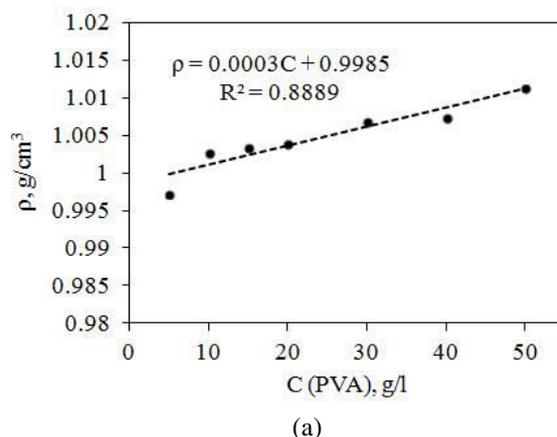
The latter is likely related to the excessive viscosity of electrolyte, causing it to remain on the surface and, possibly, inside of Ni(OH)₂/PVA composite film. When dried, such the remaining electrolyte would bind to a film as a ballast that would interfere with ion mobility inside through the film. This leads to the conclusion, that for given electrolyte and deposition method, the optimal concentration of PVA template is 40 g/l.

3.2 Study of physicochemical properties of electrolytes with different PVA concentration

3.2.1 Density measurements

Results density measurements of 0.01 M Ni (NO₃)₂ electrolytes with different PVA concentrations are shown in Figure-12a.

It can be seen, that density increases with increasing PVA concentration, with dependency being



almost linear ($R^2=0.89$). The deviation of experimental data is likely related to different PVA concentrations giving the different shape of the meniscus, which can result in an error in volume measurement when pycnometer is used.

The data can be further validated, by extrapolation the experimental curve to PVA concentration of 0 g/l, which result in a value of 0.99 g/ml. The obtained value is almost exactly as water density at 18 °C - 0, 9986 g/ml.

3.2.2 Viscosity measurements

Figure-12b shows the results of viscosity measurements for solutions with different PVA concentration and constant nickel nitrate concentration (0.01 M).

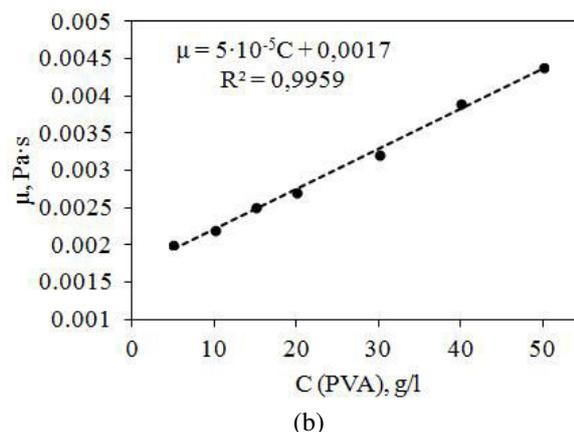


Figure-12. The dependency of electrolyte density (a) and viscosity (b) on the concentration of PVA.



The obtained results reveal that viscosity of electrolyte increases with increasing PVA concentration. Such a result is expected, as twisted polymer molecules form a polymer-water matrix which is more viscous than

water alone. The obtained dependency is almost linear which indicated by coefficient $R^2=0.99$.

3.2.3 Electrolyte conductivity

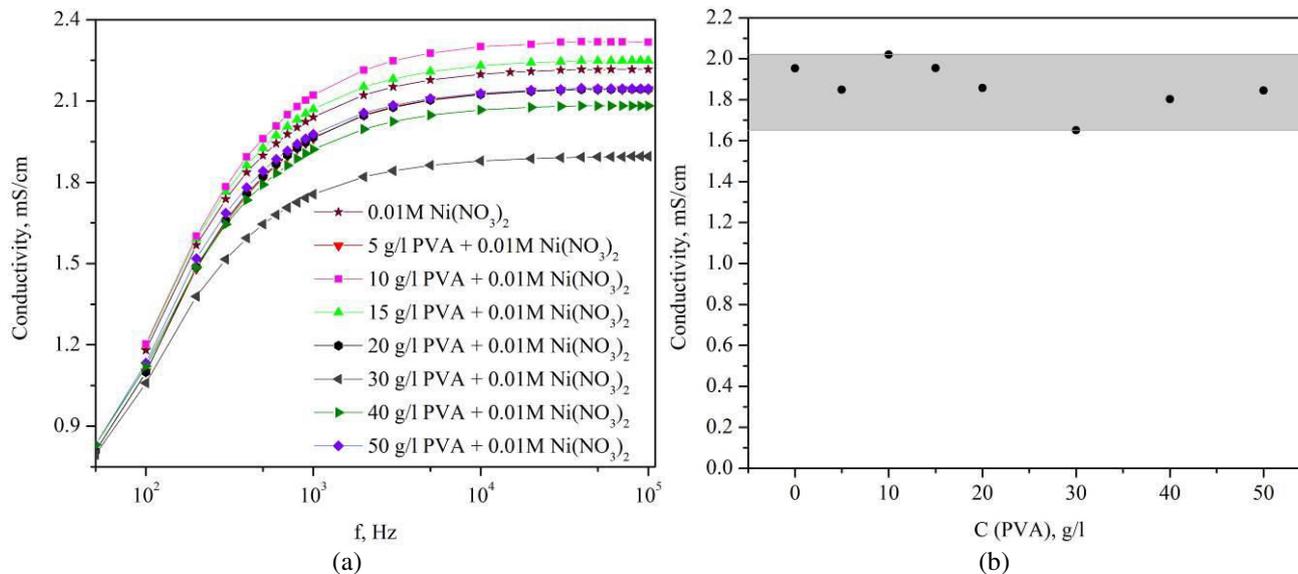


Figure-13. The dependency of electrolyte conductivity on PVA concentration measured at different frequencies of measuring current (a) measured on bridge P-5083 and dependency of conductivity on PVA concentration (b) measured with 1000 Hz current using conductometer Mettler Toledo NPC227.

Conductive is a parameter that can significantly affect kinetics and mechanism of the reaction. Thus it's of importance to measure the effect of PVA concentration on the conductivity of nickel nitrate electrolyte. According to Walden- Piszrzhewsky rule, [33, 34] the conductivity of the electrolyte is related to its viscosity. According to this, a product of viscosity and equivalent conductivity at infinite dilution is almost constant and is independent of them. While some specific factors can result in deviation from the rule, it is expected that higher viscosity of electrolyte would result in its lower conductivity.

Given that viscosity of electrolyte increases with higher PVA concentration, it is expected, that higher PVA concentrations would lead to lower conductivity. However, the experimental dependency (Figure-13a, b) is different from what was expected. In our case, the conductivity is almost independent of PVA concentration. The minor deviation is more likely related to deviation in the composition of nickel salt - $Ni(NO_3)_2 \cdot 6H_2O$, i.e. the non-uniform distribution of water molecules. Such non-uniformity resulted from water evaporation or absorption, can result in deviation from the calculated concentration of $Ni(NO_3)_2$ in solution.

However, this dependency does not contradict our assumptions. Our assumption, is that while the presence of PVA molecules in solution does increase its viscosity on a macro level, due to the formation of the network from twisted polymer molecules, the cell size is likely larger than radii of solvated ions and does not obstruct their movement. This would be why the reason as to why the effect of PVA on the viscosity of electrolyte

was affected, but its conductivity was not affected by such concentration studied concentrations of PVA.

4. CONCLUSIONS

A series of experiments were conducted in an effort to evaluate the influence of polyvinyl alcohol concentration on electrochemical and optical properties of films deposited onto FTO. Additionally, important fundamental physicochemical characteristics of electrode position electrolytes with different concentration of PVA have been studied. These characteristics can affect the rate and mechanism of reactions occurring on the electrode, and provide useful data for further development of the electrode position method. The conducted experiments have revealed that PVA template as a component of electrolyte plays a key role in the deposition of the electrochromic film.

It was discovered, that concentration of PVA has a significant effect on electrochemical and optical properties of films, by forming a polymer matrix which holds nickel hydroxide crystals [11]. This matrix ensures that nickel hydroxide has sufficient electrical contact to the substrate. This thesis is supported by experimental results of cyclic voltammetry and optical measurements. The binding properties of PVA are also reflected in a photo of cycled samples. For complex studies on properties of the electrochromic film, a series of films have been deposited from electrolytes with PVA concentration ranging from 5 - 50 g/l.

Density and conductivity measurements of electrolytes with different PVA concentration have



revealed that while density is proportional to PVA concentration, the conductivity is not affected by it. It is assumed that the size and shape of PVA globules are such that they do not obstruct ion movement, yet, they are heavy enough to affect density.

Viscosity measurements reveal a direct dependency of viscosity on PVA concentration

Study result on properties of films deposited from electrolytes with different PVA concentration has revealed that electrochemical and optical properties are improved with PVA concentration increasing from 5 to 30 g/l but start to degrade at concentrations higher than 40 g/l. This results in PVA concentration of 40 g/l being optimal among studied concentration range of 5-50 g/l. Thus there are two types of effects of PVA concentration on the properties of electrochromic films. In the range of low concentrations, the higher concentration results in stronger binding of nickel hydroxide to the substrate surface, ensuring good electrical contact and stable operation. And in range of high concentrations, the excessive PVA remains in the film, turning into insulating ballast upon drying, thus impeding ion migration and overall performance of the film.

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