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SMART WINDOWS: CATION INTERNAL AND ANION EXTERNAL ACTIVATION FOR ELECTROCHROMIC FILMS OF NICKEL HYDROXIDE

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Two methods - internal and external - were used for improving the electrochemical activity and electrochromic properties of Ni(OH)₂ films. In the case of internal activation, Al³⁺ ions were added to the electrolyte composition during the electrochemical precipitation process. In the case of external activation, [Fe(CN)₆]⁴⁻ ions were used in the electrolyte during the cycling process. In all the experiments there were used Ni(OH)₂ films synthesized by the electrochemical template method with polyvinyl alcohol (PVA) addition to the electrolyte composition. It was shown that the addition of [Fe(CN)₆]⁴⁻ ions into the electrolyte for cycling leads to significant improvement of electrochemical and electrochromic (colorization-bleaching) properties. At the same time, the addition of Al³⁺ ions into the electrolyte for Ni(OH)₂ films precipitation leads to drastic worsening of their properties. Also, possible mechanisms of Al³⁺ and [Fe(CN)₆]⁴⁻ ions influence were considered in this work.

Electrochromic devices are capable of changing their transparency under applied voltage, thus controlling heat and light transmittance. The state can be changed between bleached, colored or semi-colored. Color can vary from intense to barely noticeable. The voltage supply is only necessary for adjusting the degree of transparency, and after that, the power supply is almost unnecessary for maintenance of required state.

The electrochromic devices are based on redox reactions occurring in an electrochemical cell. Two processes occur:

- reduction of an oxidized form (the reduced form is colored):
oxidized form + electron(s) → reduced form,
- oxidation of a reduced form (the oxidized form is colored):
reduced form – electron(s) → oxidized form.

The described reactions are responsible for changes in optical properties. When voltage is turned off the system maintains its altered state. This is called “memory effect”.

The design is composed of two glasses covered with conducting films that also act as a frame, electrochromic film and an electrolyte. A polyethylene terephthalate (PET) can be used instead of glass, to design flexible devices. In most cases, the tin-doped indium oxide is used as a transparent conducting film. For modulation of incident radiation, at least one electrochromic film must be utilized in the devices’ design. A second electrochromic film can be employed to improve color intensity.

Ni(OH)₂ is one of the studied electrochromic materials. In order to employ nickel hydroxide as an electrochromic material, it’s deposited on a glass substrate covered with a conductive support. When current is applied the following reversible topochemical reaction occurs:

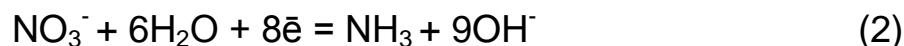


Thin films of Ni(OH)₂ change their color from transparent to dark-brown and backwards. The mechanism of electrochromic process depends on structure, presence of water in material’s pores and impurities.

Investigation methodology

The hydroxide films were cathodically electrodeposited from 1M nitrate solutions of nickel with 5% wt. PVA. In case of the internal cation activation in solution for precipitation Al(NO)₃ was added. The molar ratio between Ni and Al ions was Ni : Al – 4 : 1 [1]. Electropolished nickel plates with working are of S=4 cm² was used as a substrate. The deposition was carried out galvanostatically at current density of 0.625 mA/cm².

The hydroxide film deposition occurs according to following reactions:



where Me²⁺= Ni²⁺, Co²⁺.

Electrochemical measurements were performed using Elins P – 8 potentiostat. The change of film transparency was measured as a change in voltage drop of photoresistor that was recorded with help of analog-to-digital converter. The films were cycled in range 0—550 mV (201–751 vs. NHE) at 1mV/s in 0.1 M KOH electrolyte. For the external activation by anions for cycling 0.1 M KOH electrolytes with addition of 1.6 or 3.2 mg/l K₄[Fe(CN)₆] were used [2].

Results and discussion

In figures 1-4 cyclic voltammograms and colorization-bleaching curves of all samples are shown. As it seen from fig.1 the film which was precipitated from nickel nitrate solution with PVA has good reversibility and high depth of colorization (fig.1b). Here upper point of the colorization-bleaching curve is bleached state. Gradual decreasing of bleached state caused by nickel substrate using. Since metallic nickel has on the surface nickel oxides, the substrate can show weak electrochromic properties [3].

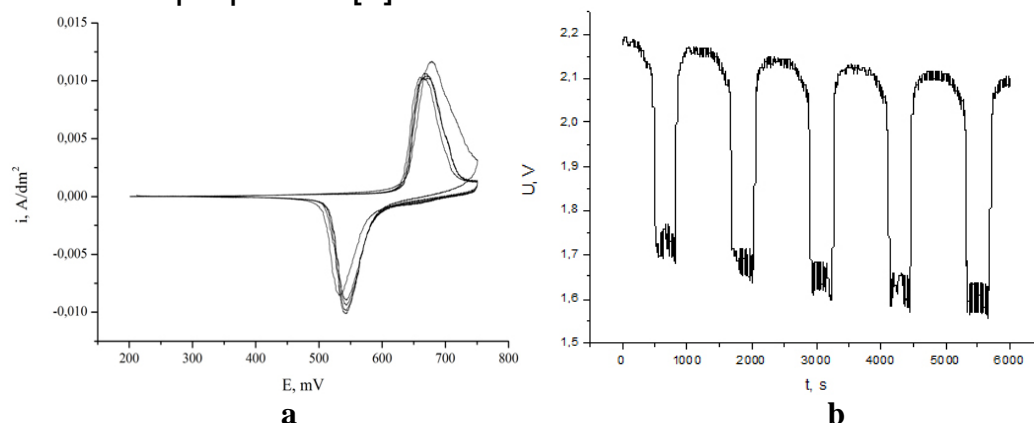


Fig.1. Cyclic voltammetry (a) and colorization-bleaching (b) curves of $\text{Ni}(\text{OH})_2$ deposited from: $1\text{M Ni}(\text{NO}_3)_2 + 5\% \text{PVA}$. Solution for cycling: 0.1 M KOH

The main idea of aluminum ions addition was in a possibility of the precipitation of the layered double hydroxides (LDHs) based on Al with higher electrochromic and electrochemical properties. However, addition of Al^{3+} in precipitation electrolyte leads to drastic worsening of both electrochemical and electrochromic properties. In the fig.2 it is seen oxidation-reduction peaks absence as well as any colorization process. Probably, the electrochemical method not fits for LDHs precipitation due to small electrogeneration speed for OH^- ions during the process. Thus, aluminum ions results to $\text{Ni}(\text{OH})_2$ poisoning, that is well known phenomena described in a literature.

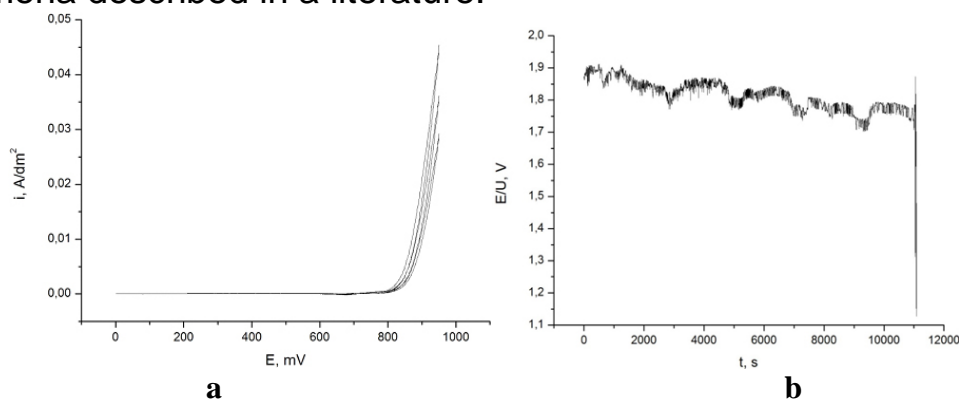


Fig.2 Cyclic voltammetry (a) and colorization-bleaching (b) curves of $\text{Ni}(\text{OH})_2$ deposited from: $1\text{M Ni}(\text{NO}_3)_2 + 0,25\text{M Al}(\text{NO}_3)_3 + 5\% \text{PVA}$. Solution for cycling: 0.1 M KOH

For activation by $[\text{Fe}(\text{CN})_6]^{4-}$ ions, $\text{K}_4[\text{Fe}(\text{CN})_6]$ salt was added to 0.1 M KOH solution, which was used for cycling. $\text{K}_4[\text{Fe}(\text{CN})_6]$ concentration in 1.6 mg/l is not lead to significant changes in depth of colorization and in electrochemical properties – fig.3, but in case of higher concentration (3.6 mg/l, fig.4) properties are increased. The depth of colorization and current peaks considerably higher than they are for $\text{Ni}(\text{OH})_2$ precipitated from $\text{Ni}(\text{NO}_3)_2$ with PVA (fig.1) and for $\text{Ni}(\text{OH})_2$ precipitated from $\text{Ni}(\text{NO}_3)_2$ with PVA and 1.6 mg/l $\text{K}_4[\text{Fe}(\text{CN})_6]$ (fig.3). The mechanism of such effect can lie in ions intercalation which open intercrystalline space for electrochemical process.

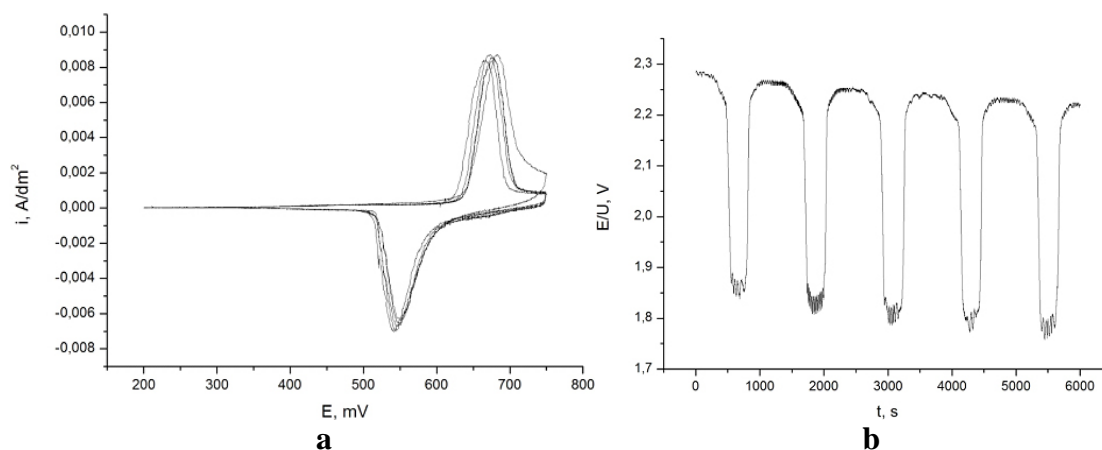


Fig.3. Cyclic voltammetry (a) and colorization-bleaching (b) curves of $\text{Ni}(\text{OH})_2$ deposited from: 1M $\text{Ni}(\text{NO}_3)_2$ +5% PVA. Solution for cycling: 0.1 M KOH + $[\text{Fe}(\text{CN})_6]^{4-}$ 1,6 mg/l

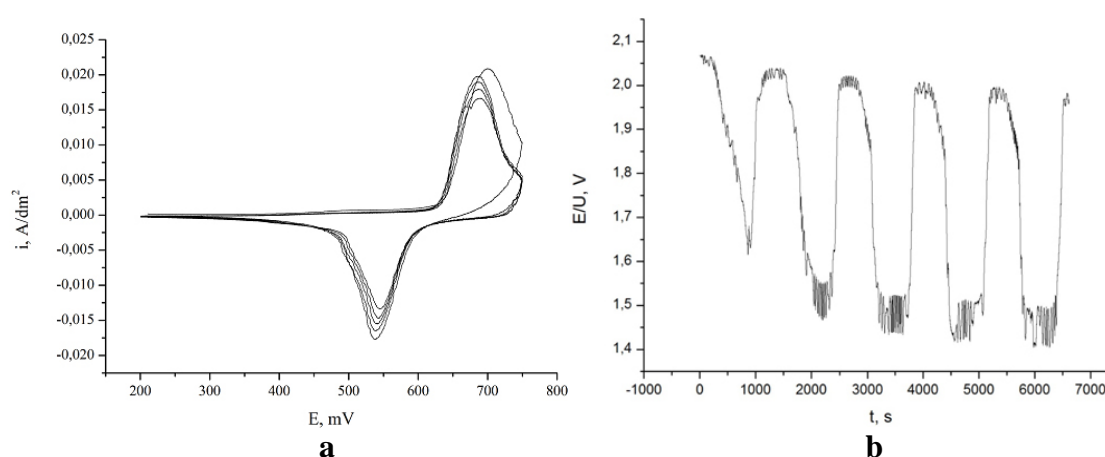


Fig.4. Cyclic voltammetry (a) and colorization-bleaching (b) curves of $\text{Ni}(\text{OH})_2$ deposited from: 1M $\text{Ni}(\text{NO}_3)_2$ +5% PVA. Solution for cycling: 0.1 M KOH + $[\text{Fe}(\text{CN})_6]^{4-}$ 3,2 mg/l

Conclusions

It were shown effects of addition of Al^{3+} in electrolyte for films $\text{Ni}(\text{OH})_2$ precipitation and $\text{K}_4[\text{Fe}(\text{CN})_6]$ ions in electrolyte for cycling. It was found two contrary effects: Al^{3+} conducts to $\text{Ni}(\text{OH})_2$ poisoning, in contrary $\text{K}_4[\text{Fe}(\text{CN})_6]$ addition leads to significant properties increasing. Activation mechanism by $[\text{Fe}(\text{CN})_6]^{4-}$ ions can lie in intercalation process of ions into intercrystalline space with simultaneous opening inner surface for electrochemical process.

References

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