



Electrochromic Properties of Nickel Hexacyanoferrate Thin Films Prepared by a Simple Chemical Deposition Method

Isak Aliji^{a*}, Julijana Velevska^b, Metodija Najdoski^c

^{a,b}University for Business and Technology – Faculty of Radiology - Kalabria, Pristina 10000, Kosovo

^bSaints Cyril and Methodius University, Faculty of Natural Sciences and Mathematics, Institute of Physics,
Arhimedova 3, Skopje 1000, Republic of N. Macedonia

^cSaints Cyril and Methodius University, Faculty of Natural Sciences and Mathematics, Institute of Chemistry,
Arhimedova 5, Skopje 1000, Republic of N. Macedonia

^aEmail: isak.aliu@hotmail.com

Abstract

In this work a simple chemical bath deposition method was developed and employed for the preparation of Nickel Hexacyanoferrate (NiHCF) films. The films were deposited by successive immersion of the fluorine doped glass substrates (FTO) into acidic aqueous solution of NiCl₂ and K₄[Fe(CN)₆]. X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Atomic force microscopy (AFM) confirmed that the obtained NiHCF films had crystalline structure. Cycling voltammetry was performed in order to investigate the electrochemical properties of the films. Visible spectra of NiHCF films were recorded *in-situ* in the both, bleached and colored state. From those spectra were estimated the optical band gaps. The response times of the bleaching and coloring was estimated to an abrupt potential change from -2 V to +2 V and reverse. The coloration efficiency was estimated from the dependence of the optical density on charge density.

Keywords: Electrochromism; Nickel Hexacyanoferrate; Chemical deposition.

* Corresponding author.

1. Introduction

A reversible change in a material's color under an applied voltage is known as Electrochromism [1-3]. Since the discovery of the phenomenon, electrochromic materials have been widely investigated, their electrochromic properties have been improved, new materials have been synthesized and electrochromic devices have been constructed.

Today electrochromic materials give opportunity for many technological applications such as smart windows [4-7], antiglare mirrors [8] displays [9], camouflages [10] and sunglasses [11]. Among them, smart windows represent a promising application because they can reduced the power consumption for lightening and air conditioning by reducing solar heat gain and provide indoor comfort by reversible color changes.

Numerous materials, inorganic and organic, exhibit electrochromic behavior, and they can be divided into two classes [12, 13]: cathodically coloring electrochromic materials which possess a reduced color state, and anodically coloring materials which possess oxidized colored state.

Among the inorganic electrochromic materials, transition metal oxides are the most investigated electrochromic materials, but recently, transition metal hexacyanoferrates have been considered in many technologies including electrochromic devices [14-17], charge storage [18-20], ion exchange [21,22], electrocatalysis [23-25] and molecular electronics and magnetism [26,27].

Transition metal hexacyanoferrate refers to iron(III) hexacyanoferrate(II) known as Prussian blue (PB) and its analogues (PBAs) [16,21]. Among the PBAs, nickel(II) hexacyanoferrate(II,III) (NiHCF) films exhibit attractive redox properties in terms of the model electroactivity and the related sorption of electrolyte cations [28].

The electrochemical behavior of transition metal hexacyanoferrates heavily depends on the structure and composition of the film, which on the other hand depend on the synthesis method and deposition conditions [29].

The aim of this work is to investigate electrochromic properties of NiHCF thin films prepared by a simple chemical method.

2. Materials and methods

2.1. Deposition of the thin films

NiHCF thin films have been deposited onto commercially fluorine doped tin oxide (FTO) coated glass substrates with dimensions of 50x20 mm and electric resistance of 10 – 20 Ωcm^{-2} . Before the deposition, the substrates have passed a cleaning process which is described in our previous work [17]. The deposition of the films was carried out at room temperature from two solutions: aqueous solution of nickel(II) chloride, and aqueous solution of potassium hexacyanoferrate(II). The 0.1 M nickel(II) chloride solution was prepared by weighing 2.379 g of nickel(II) chloride hexahydrate, dissolving in 100 ml volumetric flask in approximately 50 ml deionized water, and after dissolving, it was diluted up to desired volume of 100 ml. The 0.1 M stock solution

of potassium hexacyanoferrate(II) with volume of 100 ml was prepared in similar way by dissolving 4.224 g of potassium hexacyanoferrate(II) trihydrate in about 50 ml deionized water in 100 ml volumetric flask, and after dissolving, it was diluted up to 100 ml. Previously cleaned substrate has been immersed in the first solution, and after 2-3 s in the second solution, where it stays for the same time. The two immersions have been counted as one deposition cycle. The film thickness depends on the number of deposition cycles and can be control by counting the immersions of the substrate in one of the solutions. The detailed deposition procedure is previously described in our work [17] for deposition of cobalt(II) hexacyanoferrate(II,III) thin films. The obtained NiHCF thin films were transparent. Two kind of samples prepared with 100 and 200 deposition cycles have been investigated. The thickness of the films was 590 nm and 1100 nm corresponding to 100 and 200 cycles respectively, with average increase in the growth in the film thickness in one deposition cycle of 5.7 nm.

2.2. Characterization of the films

The XRD patterns of the NiHCF thin films have been recorded by RigakuUltima IV X-ray powder diffraction instrument, where $\text{CuK}\alpha$ radiation has used in the 2θ range of 5° - 70° . The thickness and the surface morphology of the films have been observed by Tescan Vega 3 LMU Scanning Electron Microscope. Shimadzu Scanning Probe Microscope SPM-9700 has been used in dynamic mode at room temperature for taking AFM micrographs. The chemical identification has been conducted using Oxford X-act EDS. The samples for SEM and EDS analysis have been gold coated using Quorum, Q150R ES Rotary Pumped Coating System.

A cyclic voltammetry was employed for the electrochemical measurements, using AUTOLAB II equipment (Eco-Chemie, Utrecht, Netherlands) in the potential range between -0.7 V and -0.2 V. A conventional three electrode system consisted of NiHCF/FTO as working electrode, Pt wire as counter electrode, KCl-saturated Ag/AgCl as reference electrode and 0.1M KCl aqueous electrolyte, has been used for examination of the electrochemical properties of the films. The working area of the film was 0.8 cm^2 , and the potential scan rate was 10 mV/s. The optical spectra of the NiHCF thin films in the both, bleached and colored states, have been recorded using Varian Cary 50 Scan Spectrophotometer in the range from 350 nm to 900 nm. The films have been colored and bleached using +2 V and -2V respectively. The coloring and the bleaching of the films have been performed in an electrochromic, two-electrode glass, home-made cell, consisted of NiHCF/FTO and blank FTO as electrodes, and 1M KCl aqueous solution as an electrolyte. An electrochromic cell with two clean FTO substrates filled with electrolyte has been measured as 100% background. Sequential potential ($\pm 2 \text{ V}$) have been carried out for response time calculations.

3. Results and discussion

The NiHCF thin films investigated in this work revealed electrochromic behavior, repeatedly changing color from transparent to yellow by alternative application of a negative and positive voltage respectively. Fig. 1 presents ex-situ photographs of NiHCF film in (a) bleached and (b) colored states. After bleaching (coloring), the film was removed from the electrochromic cell, rinsed in distilled water, dried and then photographed with a digital camera.

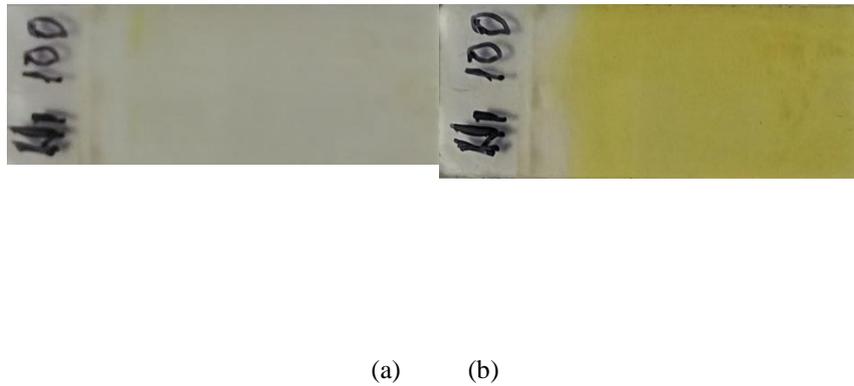


Figure 1: Ex-situ photographs of chemically deposited NiHCF film in (a) bleached and (b) colored states

The diffraction patterns of the blank FTO substrate and NiHCF film deposited on FTO substrate are presented in Fig. 2., The diffraction peaks at 17.680° , 25.100° and 35.780° 2θ values belong to NiHCF (JCPDS No. 51-1897), while the other intensive peaks denoted with asterisk belong to SnO_2 from the FTO substrate (JCPDS No. 46-1088). These results confirm creation of NiHCF films onto FTO substrate [30]. As can be seen, all the peaks related to NiHCF represent a typical face-centered structure [31, 32]. According to the diffractogram, the lattice constant has been evaluated as 10.035 \AA .

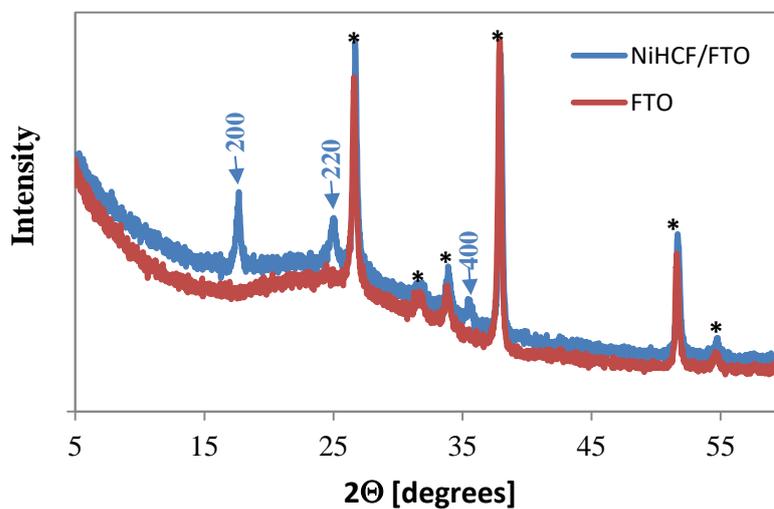


Figure 2: XRD patterns of the blank FTO substrate and NiHCF film deposited on FTO substrate

Scanning electron microscopy (SEM) was employed for investigation of the surface morphology of the chemically deposited NiHCF films. The SEM microphotograph is shown in Fig. 3. It illustrates two dimensional image of film with relatively rough surface, formed of well-defined crystallites or crystal clusters with dimensions between 80 nm - 800 nm. It should be noted that some cracks also appeared on the surfaces, and this

seemed to be the common phenomenon due to the shrinkage of film whilst it was dried [33]. The same result has been obtained from the AFM microphotograph (Fig. 4).

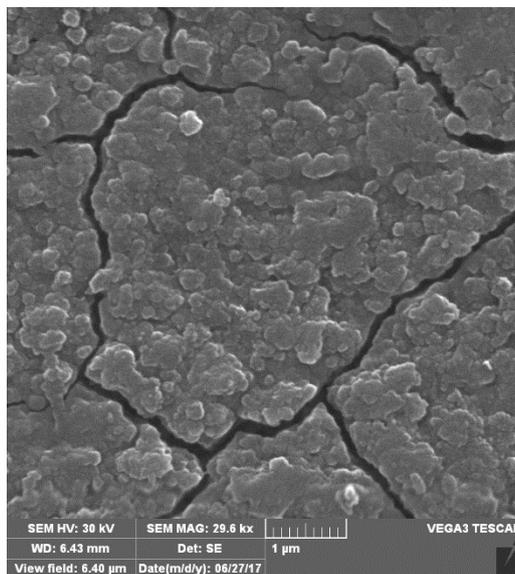


Figure 3: SEM microphotograph of the chemically deposited NiHCF film

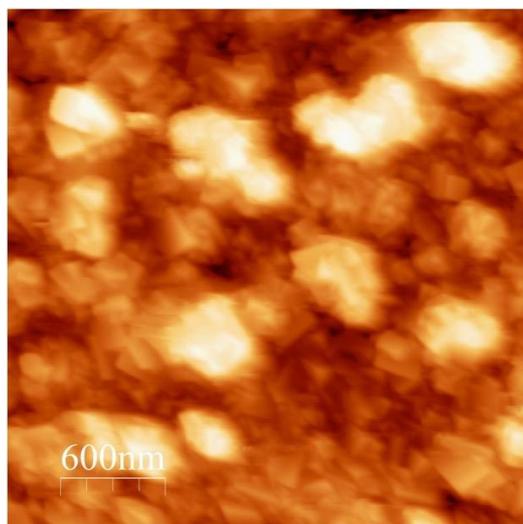


Figure 4: AFM microphotograph of the chemically deposited NiHCF film

Electrochemical behavior of the NiHCF films has been investigated by cyclic voltammetry (CV). The cyclic voltammograms of NiHCF films with two different thicknesses (590 and 1100 nm) are presented in Fig. 5.

The cyclic voltammograms of NiHCF films recorded in solutions which contain K^+ ions, usually have two pairs of re-dox peaks [28, 34]. The presence of the two pairs has been ascribed to existence of two stable forms of NiHCF: soluble and insoluble. The pair of peaks which occurs at more positive potentials is related to the soluble form of NiHCF, and the other pair is related to the insoluble form. The corresponding red-ox reactions can be represented by the equations:



for the soluble form, and



for the insoluble form of NiHCF.

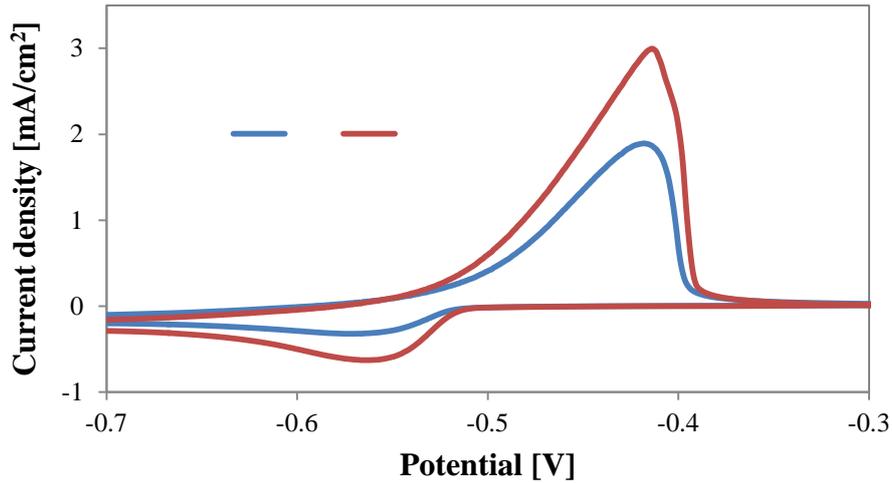


Figure 5: Cyclic voltammograms for 590 nm and 1100 nm thick NiHCF films

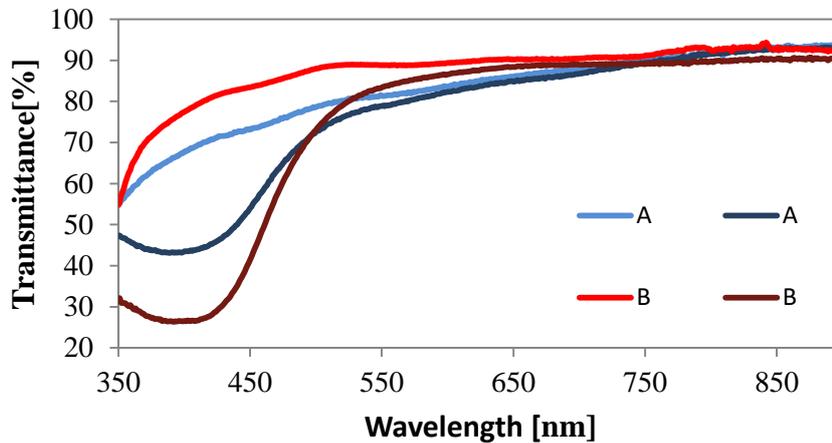


Figure 6: Visible transmittance spectra of 590 nm (A) and 1100 nm (B) thick NiHCF films

As can be seen from the Fig. 5, the chemically deposited NiHCF films investigated in our work have only one well defined pair of red-ox peaks which corresponds to insoluble form of NiHCF. Similar situation have been observed in [35]. The absence of the soluble form indicates that the bleaching (reduction) and the coloring (oxidation) of the chemically deposited NiHCF films takes place according to the equation (2). Another characteristic feature is the higher anodic peak current than the cathodic one which could be ascribed to an

electrocatalytic oxidation [36].

Fig. 6 presents the in-situ optical transmittance spectra in the wavelength range from 350 nm to 900 nm in both, bleached and colored states of the films. As can be seen, the spectra show maximum transmittance difference about 25% and 58% for 590 nm and 1100 nm thick NiHCF films respectively, at around 400 nm.

The optical transmittance spectra have been used to estimate the optical band gaps E_g of the films. The optical band gaps were estimated from the absorption coefficient α by fitting the data to the relation.

$$\alpha h\nu = B(h\nu - E_g)^m \quad (3)$$

where the absorption coefficient α was calculated from the transmittance data (T) and film thickness (t) by the equation:

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \quad (4)$$

and B is the constant, $h\nu$ is the energy of the incident photon and m is a number which determines the type of electron transition causing the absorption [37].

Fig. 7 shows the plots of $(\alpha h\nu)^2$ versus $h\nu$ in both, the bleached and the colored states of 590 nm thick (A) and 1100 nm thick (B) NiHCF films. The optical band gaps were calculated from the linear parts as intercepts with the photon energy axes, and the obtained results are presented in Table 1.

Table 1: Optical band gaps estimated from the linear parts as intercepts with the photon energy axes,

Thickness (nm)	State	E_g (eV)	R^2
590	Bleached	2.98	0.987
	Colored	2.53	0.996
1100	Bleached	3.01	0.981
	Colored	2.62	0.999

The coloration efficiency η of the NiHCF films was calculated from the dependence of the optical density change: $\Delta OD = \ln(T_b/T_c)$ on charge density $\Delta Q/A$ at 400 nm (wavelength of the maximum transmittance difference) during the coloration after the films were fully bleached:

$$\eta = \frac{A \ln(T_b/T_c)}{\Delta Q} \quad (5)$$

where T_b and T_c are transmittance of the fully bleached and colored states respectively, ΔQ is the injected/ejected charge during the coloration process and A is the active area of the electrochromic film. Fig. 8 presents the plot of the optical density change against the charge density. The coloration efficiency at 400 nm was determined as the slope from the line fitted to the linear part of the curve. The estimated η values have been found to be 13.9 and 23.7 cm²C⁻¹ for the 590 nm and 1100 nm respectively. The obtained results showed increasing of the coloration efficiency with increasing of the thickness for the chemically deposited NiHCF films.

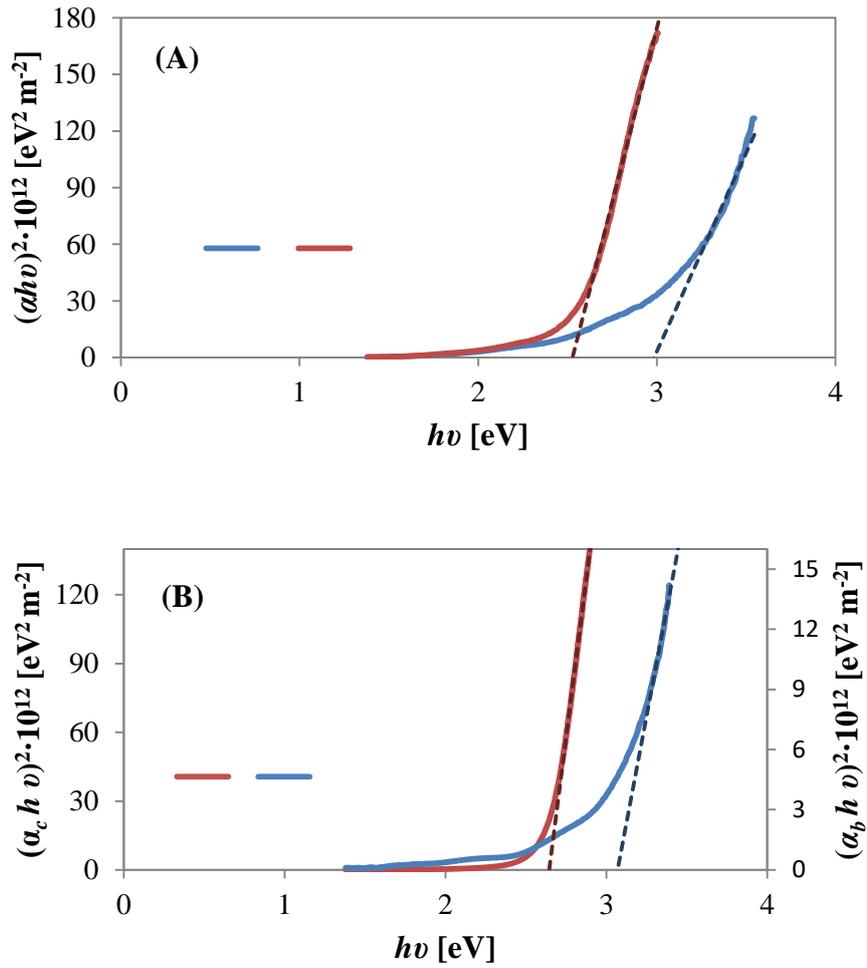


Figure 7: The plots of $(ahv)^2$ versus photon energy (hv) for chemically deposited 590 nm (A), and 1100 nm (B) thick NiHCF films

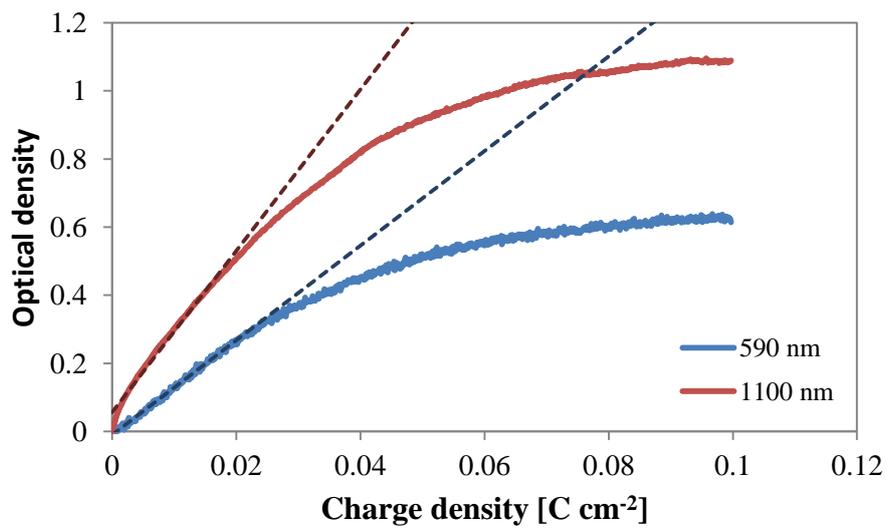


Figure 8: The dependence of the optical density change on the charge density at a wavelength of 400 nm

In order to examine the response time, the time dependence of transmittance (T) at 400 nm due to the abrupt potential (U) change between ± 2 V was recorded in-situ and presented in Fig. 9 and Fig. 10. The response times of coloring and bleaching was determined as the time needed for the film to reach 80% of the final change in the transmittance. The response times were found to be 48 s for coloring and 42.9 s for bleaching for the 590 nm thick film, and 35 s for coloring and 43.5 for bleaching for the 1100 nm thick film. As can be seen, the chemically deposited NiHCF films showed decreasing of the response time with increasing of the thickness in the coloring process, while in the bleaching process it is almost constant.

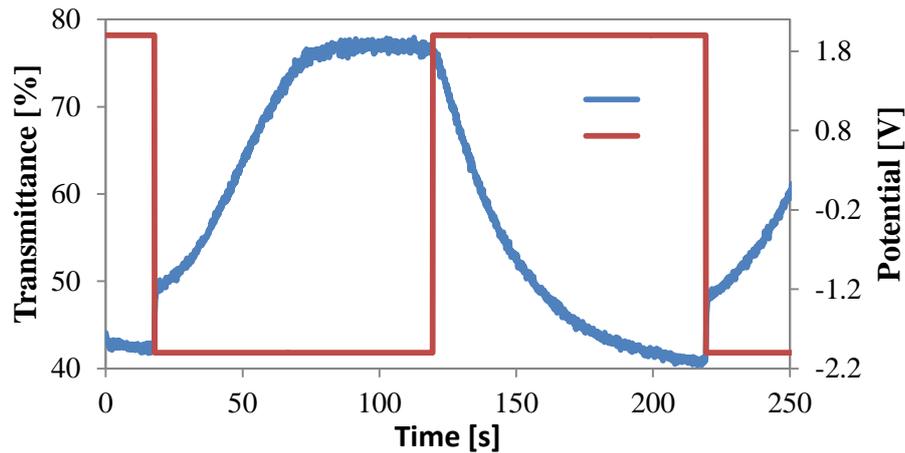


Figure 9: The time response of the transmittance at 400 nm during one cycle of bleaching and coloring of NiHCF film with thickness of 590 nm

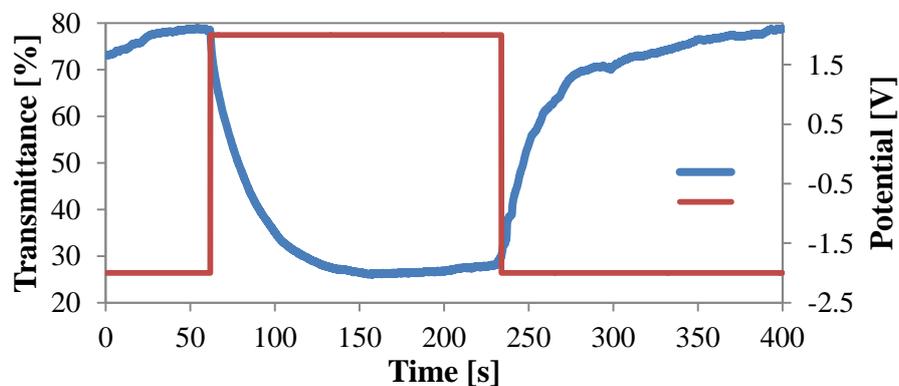


Figure 9: The time response of the transmittance at 400 nm during one cycle of bleaching and coloring of NiHCF film with thickness of 1100 nm

4. Conclusions

This work presents the investigation on electrochromism of nickel hexacyanoferrate (NiHCF) films. For that purpose new chemical method for deposition was developed. The designed method is simple, economical, do not required sophisticated equipment, offer a possibility for large area deposition and yield stable, adherent, uniform and hard films with good reproducibility by a relatively simple process. The films were chemically

deposited at room temperature from two solutions onto fluorine doped tin oxide (FTO) coated glass substrates. The investigation were conducted with films with two different thickness of 590 nm and 1100nm. Obtained films exhibited anodic electrochromism changing color from transparent to yellow. The X-ray diffraction (XRD) patterns showed that the films have typical face-centered cubic (fcc) structure. The evaluated lattice constant was .10.035 Å. The cyclic voltammetry (CV) showed a clear redox reaction, indicating switching between reduced (transparent) and oxidized (colored) states of the films. The anodic peak current was bigger than the cathodic one which could be ascribed to an electrocatalytic oxidation. The optical transmittance spectra in the wave range from 350 - 900 nm showed maximum transmittance difference about 25% and 58% for 590 nm and 1100 nm thick NiHCF film at around 400 nm. The optical transmittance spectra were also used to estimate the optical band gaps. The coloration efficiency of the films was calculated at 400 nm (maximum transmittance difference) and the obtained results showed increasing with increasing of the film thickness. The response times of the coloring and bleaching to an abrupt potential changed from -2 V to +2 V and reverse, determined as the time needed for the film to reach 80% of the final change in the transmittance. According to this criterion, the response time decreases with increasing of the film thickness in the coloring process, and it is almost constant in the bleaching process.

References

- [1] C. G. Granqvist, *Handbook of Inorganic Electrochromic Materials*, Elsevier, Amsterdam, 1995.
- [2] P. R. Somani, S. Radhakrishnan, "Electrochromic materials and devices: present and future", *Materials Chemistry and Physics*, vol.77, pp. 117-133, 2002.
- [3] J. Wang, X. W. Sun, Z. Jiao, "Application of Nanostructures in Electrochromic Materials and Devices: Recent Progress", *Materials (Basel)*, vol. 3(12), pp. 5029-5053, Nov. 2010, doi:103390/ma3125029,
- [4] J.S.E.M. Svensson, C. G. Granqvist, "Electrochromic tungsten oxide films for energy efficient windows" *Solar Energy Materials*, vol.11, pp 29-34, October, 1984, doi: 10.1016/0165-1633(84)90025.
- [5] E. S.Lee and D. L.Di Bartolomeo, "Application issuesfor large-area electrochromic windows in commercial buildings", *Sol. Energy Mater. Sol. Cells*, vol.71, pp 465-491, 2002, doi: 10.1016/So927-0248(01)00101-5.
- [6] R.Baetens, B. P.Jelle and A.Gustavsen, "Properties, requirements and possibilities of smart windows for dynamic daylight and solar energy control in buildings: a state-of-the-art review", *Sol. Energy Mater. Sol. Cells*, vol. 94, pp 87-105, 2010, doi: 10.1016/j.solmat.2009.08.021.
- [7] J.Barrat and K,Dowd, "A New Airplane for a New World: The Boeing 787 Dreamliner", *Des. Manag. Rev.*, vol. 17, pp 25-30, 2010, doi: 10.1111/j.1948-7169.2006'tb00059.x
- [8] R. J.Mortimer, "Electrochromic materials",*Chem. Soc. Rev.*, vol 26, pp 147-156,1997, doi: 10.1039/CS9972600147.

- [9] P.Anderson, R.Forchheimer, P.Tehrani and M.Berggren, "Printable All-Organic Electrochromic Active-Matrix Displays", *Adv. Funct. Mater.* vol. 17, pp3074-3082, 2007, doi: 10.1002/adfm.200601241.
- [10] P.Chandrasekhar, B. J.Zay, D.Ross, T.Mc Queeney, G. C.Birur, T.Swanson, L Kaudr. and D.Douglas, "Far-IR-trough-Visible Electrochromics Based on Conducting Polymers for Spacecraft Thermal Control and Military Uses: Application in NASA's S15 Microsatellite Mission and Military Camouflage", *American Chemical Society ACS Symposium Series* vol. 888, pp 66-79, 2005, Chapter doi: 10.1021/bk-2005-0888.ch.005.
- [11]A. M.Osterhoim, D. E.Shen, J. A.Kerszulis, R. H.Bulloch, M.Kuepfert, A. L.Dyer and J. R.Reynolds, "Four Shades of Brown: Tuning of Electrochromic Polymer Blends Toward High-Contrast Eyewear" *ACS Appl. Mater. Interfaces* vol. 7 pp 1413-1421, 2015,doi: 10.1021/am507063d
- [12]C.R. Korosec, P. Bukovec, "Sol-gel prepared NiO thin films for electrochromic application", *ActaChim. Slov.*, vol. 53, pp 136-147, 2006.
- [13] P.M.S. Monk, R.J. Mortimer and D.R. Rosseinsky, "*Electrochromism: Fundamentals and Applications*", VHC: Weinheim, 1995
- [14] R.J. Mortimer, "Five Color Electrochromicity Using Prussian Blue and Nafion/Methyl Viologen Layered Films", *J. Electrochem. Soc.*vol. 138(2), pp 633-634, 1991, doi: 10.1149/1.2085647.
- [15] M.Pyrasch, A.Toutianoush, W. Q.Jin, J.Schnepf and B.Tieke, "Self-assembled Films of Prussian Blue and Analogues: Optical and Electrochemical properties and Application as Ion-Sieving Membranes" *Chem. Mater.*,vol. 15, pp 245-254, 2003, doi: 10.1021/cm021230a.
- [16] E.Kholoud, H.Watanabe, A.Takahashi, M. M.Emara, B. A.Abd-El-Nabey, K.Tajima, and T.Kawamoto, "Cobalt hexacyanoferrate nanoparticles for wet-processed brown-bleached electrochromic devices with hybridization of high-spin/low-spin phases", *J. Mater. Chem. C*, vol.5, pp 8921-8926, 2017, doi:/10.1039/C7TC02576A
- [17] I.Aliji, M.Najdoski and J.Velevska, "A Simple Chemical Method for Deposition of Electrochromic Cobalt Hexacyanoferrate Thin Films", *International Journal of Sciences: Basic and Applied Research (IJSBAR)* vol. 40(1) pp 242-257, 2018.Available:<https://core.ac.uk/download/pdf/249336401.pdf>
- [18] Neff V. D., "Some Performance Characteristics of a Prussian Blue Battery" *J. Electrochem. Soc.*, vol. 132(6), pp 1382-1384, 1985, doi: 10.1149/1.2114121.
- [19] M.Kaneko and T.Okada, "A secondary battery composed of multilayer Prussian Blue and its reaction characteristics" *J. Electroanal. Chem.*, vol. 255, pp 45-52, 1988, doi: 10.1016/0022-0728(88)80003-2
- [20] S.Kalwellis-Mohn and E. W.Grabner, "A secondary cell based on thin layers of zeolite-like nickel

- hexacyanometallates”, *Electrochim. Acta* vol. 34, pp 1265-1269, 1989, doi: 10.1016/0013-4686(89)87169-5
- [21] L. M.Siperko and T.Kuwana, “Electrochemical and Spectroscopic Studies of Metal Hexacyano-metalate Films”, *J. Electrochem. Soc.* vol. 130, pp 396-402, 1983, doi: 10.1149/1.2119718
- [22] H.Kahlert, S.Komorsky-Lovric, M.Hermes and F.Scholz, “A Prussian blue-based reactive electrode (reactrode) for the determination of thallium ions” *J. Anal. Chem.* vol. 356, pp 204-208, 1996
- [23] V. D.Neff, “Electrochemical oxidation and reduction of thin films of Prussian blue”, *J. Electrochem. Soc.* vol. 125, pp 886-887, 1978, doi: 10.1149/1.2131575
- [24] D.Zhang, K.Wang, D. C.Sun, X. H. Xia and H. Y.Chen, “Ultrathin Layers of Densely Packed Prussian Blue Nanoclusters Prepared from a Ferricyanide Solution” *Chem. Mater.* vol. 15, pp 4163-4165, 2003, doi: 10.1021/cm034594r
- [25] P.Wang, Y. Yuan, X. Y. Jing and G. Y. Zhu, “Amperometric determination of thiosulfate at a surface-renewable nickel(II) hexacyanoferrate-modified carbon ceramic electrode”, *Talanta*, vol. 53, pp 863-869, 2001, doi: 10.1016/S0022-3541(00)00574-9
- [26] V. Escax, A. Bleuzen, J. P. Itie, P. Munsch, F. Varret and M. Verdager, “Nature of the Long-Range Structural Changes Induced by the Molecular Photoexcitation and by the Relaxation in the Prussian Blue Analogue $\text{Rb}_{1.8}\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.3} \cdot 13\text{H}_2\text{O}$. A Synchrotron X-ray Diffraction Study” *J. Phys. Chem. B*, vol. 107 (20), pp 4763-4767, 2003, doi: 10.1021/jp0340313
- [27] P. J.Kulesza, M. A.Malik, M.Berrettoni, M. Giorgetti, S.Zamponi, R.Schmidt and R.Marassi, “Electrochemical Charging, Counteraction Accommodation, and Spectrochemical Identity of Microcrystalline Solid Cobalt Hexacyanoferrate”, *J. Phys. Chem. B*, vol. 102 (11), pp 1870-1876, 1998
- [28] S.Zamponi, M.Berrettoni, P. J.Kulesza, K.Miecznikowski, M. A.Malik, O.Makowski and R.Marassi, “Influence of experimental conditions on electrochemical behavior of Prussian blue type nickel hexacyanoferrate film”, *Electrochim. Acta*, vol. 48 pp 4261-4269, 2003, doi: 10.1016/j.electacta.2003.08.001
- [29] M.Ciabocco, “Synthesis and characterization of metal-hexacyanometallates as innovative materials for analytical and technological applications” PhD thesis, Universita di Bologna, Bologna, Italy, 2017.
- [30] X. Hao, T. Yan, Z. Wang, S. Liu, Z. Liang, Y. Shen and M. Pritzker, “Unipolar pulse electrodeposition of nickel hexacyanoferrate thin films with controllable structure on platinum substrates” *Thin Solid Films*, vol. 520 (7) pp 2438-2448, Jan. 2012, <https://doi.org/10.1016/j.tsf.2011.10.005>
- [31] V.Jassal, U.Shanker and S.Shankar, “Synthesis characterization and applications of nanostructured

- metal hexacyanoferrates: a review”, *J. of Environ. Anal. Chem.*, vol. 2(2), 2015, doi: 10.4172/2380-2391.1000128
- [32] C.D.Wessels, S.V.Peddada, R.A. Huggins and Y.Cui, “Nickel hexacyanoferrate nanoparticle electrodes for aqueous sodium and potassium ion batteries” *Nano Letters* vol. 11 pp 5421-5425, 2011
- [33] S.Karnjanakom, Y.Ma, G.Guan, P.Phanthong, X.Hao, X.Du, C.Samart, A.Abuliti, “Fabrication of nickel hexacyanoferrate film on carbon fibers by unipolar pulse electrodeposition method for electrochemically switched ion exchange application” *Electrochim.Acta*, vol. 139, pp 36–41, 2014, <https://doi.org/10.1016/j.electacta.2014.06.136>
- [34] W. A. Steen, S.W.Han, M.Q.Yu, R.A Gordon., J.O.Cross, E.A.Stern, G.T.Seidler, K.M.Jeerage and D.T.Schwartz, “Structure of Cathodically Deposited Nickel Hexacyanoferrate Thin Films Using XRD and EXAFS”, *Langmuir*, vol. 18 pp 7714-7721, 2002, <https://doi.org/10.1021/la020352e>
- [35] W.Chen, H.J.Tang and X.H.Xia, “A simple method for fabrication of sole composition nickel hexacyanoferrate modified electrode and its application”, *Talanta*, vol. 80, pp 539-543, 2009, <https://doi.org/10.1016/j.talanta.2009.07.022>
- [36] Y.Wang, Y.Rui, F.Li and M.Li, “Electrodeposition of nickel hexacyanoferrate/layered double hydroxide hybrid film on the gold electrode and its application in the electroanalysis of ascorbic acid”, *ElectrochimicaActa*, vol 117 pp 398-404, Jan. 2014, <https://doi.org/10.1016/j.electacta.2013.11.141>
- [37] R.Neskovska, M.Ristova, J. Velevska and M.Ristov, “Electrochromism of the electroless deposited cuprous oxide films”, *Thin Solid Films*, vol. 515, pp 4717-4721, 2007, doi: 10.1016/j.tsf.2006.12.121