

TICKNESS – DEPENDENT AND ELECTROCHROMIC PROPERTIES OF CHEMICALLY DEPOSITED NICKEL OXIDE FILMS

J. Velevska¹, M. Pecovska - Gjorgjevich¹, M. Najdoski² and N. Stojanov¹

¹*Institute of Physics, Faculty of Natural Sciences and Mathematics,
P.O. Box 162, 1001 Skopje, Macedonia*

²*Institute of Chemistry, Faculty of Natural Sciences and Mathematics,
P.O. Box 162, 1001 Skopje, Macedonia*

Abstract. Thickness – dependent and electrochromic properties of chemically deposited Ni oxide films were investigated as a function of growth time using in situ transmittance measurements. For that purpose an electrochromic test device was constructed by using Ni oxide films as working electrodes, and fluorine doped tin oxide (FTO) coated glass as counter electrode in alkaline medium of 0.1 M NaOH aqueous solution. The obtained Ni oxide films exhibited anodic electrochromism, changing color from transparent to dark brown. By increasing the thickness of the Ni oxide, the transmittance or optical differences during coloring/bleaching process were increased. In this work were investigated the dependence of the optical density change, coloration efficiency and the electrochromic response time as a function of growth time.

PACS: 81.15 Lm, 85.80 Dg

1. INTRODUCTION

Electrochromic materials are able to change their optical properties reversibly and persistently, by the application of an electric voltage. These materials can be integrated in multilayer EC devices capable of modulating transmittance, reflectance, thermal emittance, and scattering, thus opening avenues for new applications in optical technology, including smart windows for energy efficiency architecture [1, 2]. An electrochromic device consists of a transparent electrically conducting layer, an electrochromic cathodic coloring material, an ion conducting electrolyte, and an electrochromic anodic coloring material. Tungsten oxide is currently widely used as an electrochromic cathodic coloring material, and indium tin oxide (ITO), or fluorine doped tin oxide (FTO) is used for transparent conducting layer. Nickel oxide represents a promising material for use in complementary anodic coloration [1, 2, 3, 4]. There are various methods for the growth of nickel oxide films such as cathodic electrodeposition [5], sputtering [6], chemical vapor deposition [7], spray pyrolysis [8], sol-gel technique [9], etc.

In order to obtain optimized maximum optical attenuation of the complementary electrochromic device, charge capacities on both electrochromic layers must be balanced [10]. Typically, the amount of the charge capacity of the electrochromic layer can be controlled by adjusting thickness via the growth time used in the process of deposition. However, despite the importance of the thickness, little systematic research has been reported regarding this issue [11, 12]. In this article electrochromic properties of chemically deposited nickel oxide films were investigated as a function of film thickness or growth time by *in situ* transmittance measurements.

2. EXPERIMENTAL

In this work, nickel oxide films with different thickness were prepared by chemical deposition technique onto fluorine doped tin oxide (FTO) coated glass substrates. This technique is simple and does not required special set-up. A laboratory beaker was used for deposition on four substrates. An aqueous solution containing 1g $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and 4g urea in 50 cm^3 deionized water was placed in the beaker. Then the substrates were vertically introduced into the solution. The temperature of the solution was adjusted and kept at 95⁰ C. The solution reached this temperature within 15 min. We stirred the solution occasionally. The first substrate was taken out 25 min from the beginning (10 min after the reaching temperature of 95⁰ C), the second one was taken out 30 min from the beginning (15 min after the reaching temperature of 95⁰ C), and the third one was taken out 35 min from the beginning (20 min after the reaching temperature of 95⁰ C). The fourth substrate was heating 45 min in one bath (30 min after the reaching temperature of 95⁰ C), and 45 min in another bath.

All the electrochemical potential cycling was performed using an electrochromic test device (Fig. 1). It consisted of a transparent cuvette with 0.1 M NaOH aqueous solution electrolyte in which two electrodes were immersed. The working electrode represented the nickel oxide thin film onto FTO coated glass, whereas counter electrode was FTO coated glass.

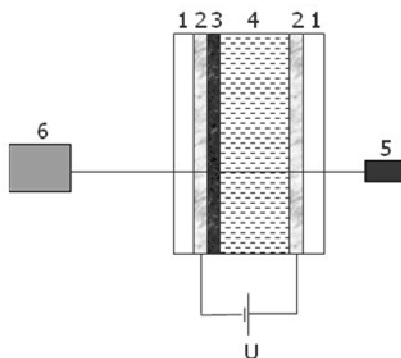


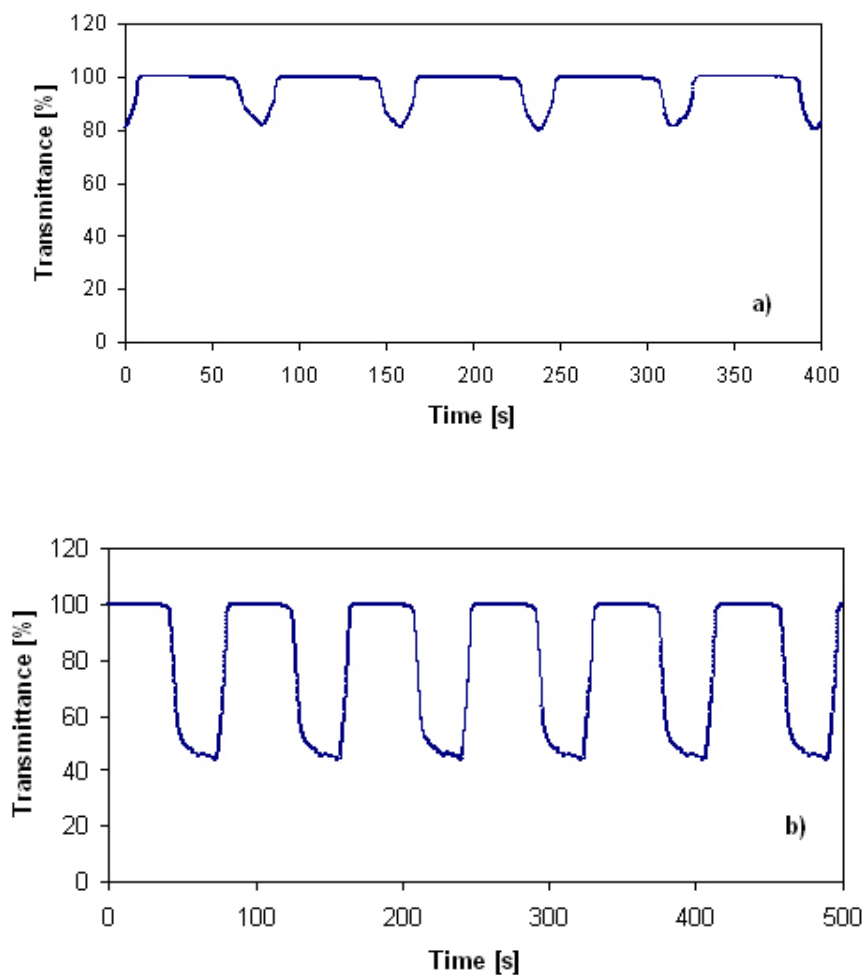
Fig. 1. Cross-section of the ECTD: 1 – glass, 2 – FTO, 3 – nickel oxide film, 4 – electrolyte, 5 – light source, 6 – light detector.

The transmittance was simultaneously measured *in situ* during all experiments. The *in situ* transmittance measurement technique represents optical behavior as a function of time

during the coloring/bleaching process of the electrochromic active film and provides better understanding of differences in optical performance between all samples. The response time of the electrochromic nickel oxide films was determined by applying a pulse potential wave between -3 V and +3 V. All transmittance measurements were carried out with white light. The transmittance (%*T*) of the FTO/glass with the electrolyte and the cell window was assumed to be 100%.

3. RESULTS AND DISCUSSION

Fig. 2 shows the transmittance curves during the pulse potential cycling test between -3 V and +3 V of the nickel oxide films grown for 10 min (a), 15 min (b), 20 min (c) and 60 min (d).



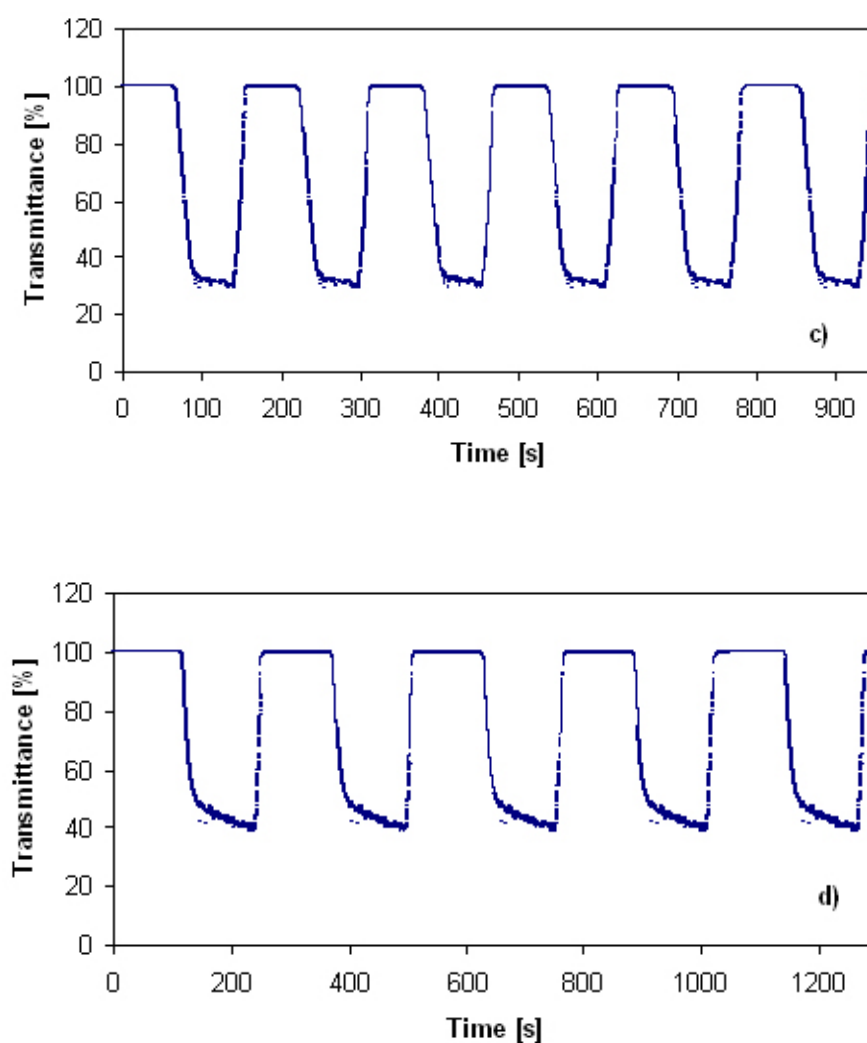


Fig. 2. : Pulse potential curves for chemically deposited Ni oxide films grown for 10 min a), 15 min b), 20 min c) and 60 min d).

As one can see, all samples showed a stable pulse potential cycling performance. With increasing growth time, the transmittance difference ($\Delta T = T_{\text{bleached}} - T_{\text{colored}}$) between the bleached and colored state increased, except for the thickest film because the maximum bleached transmittance decreased for the thick samples.

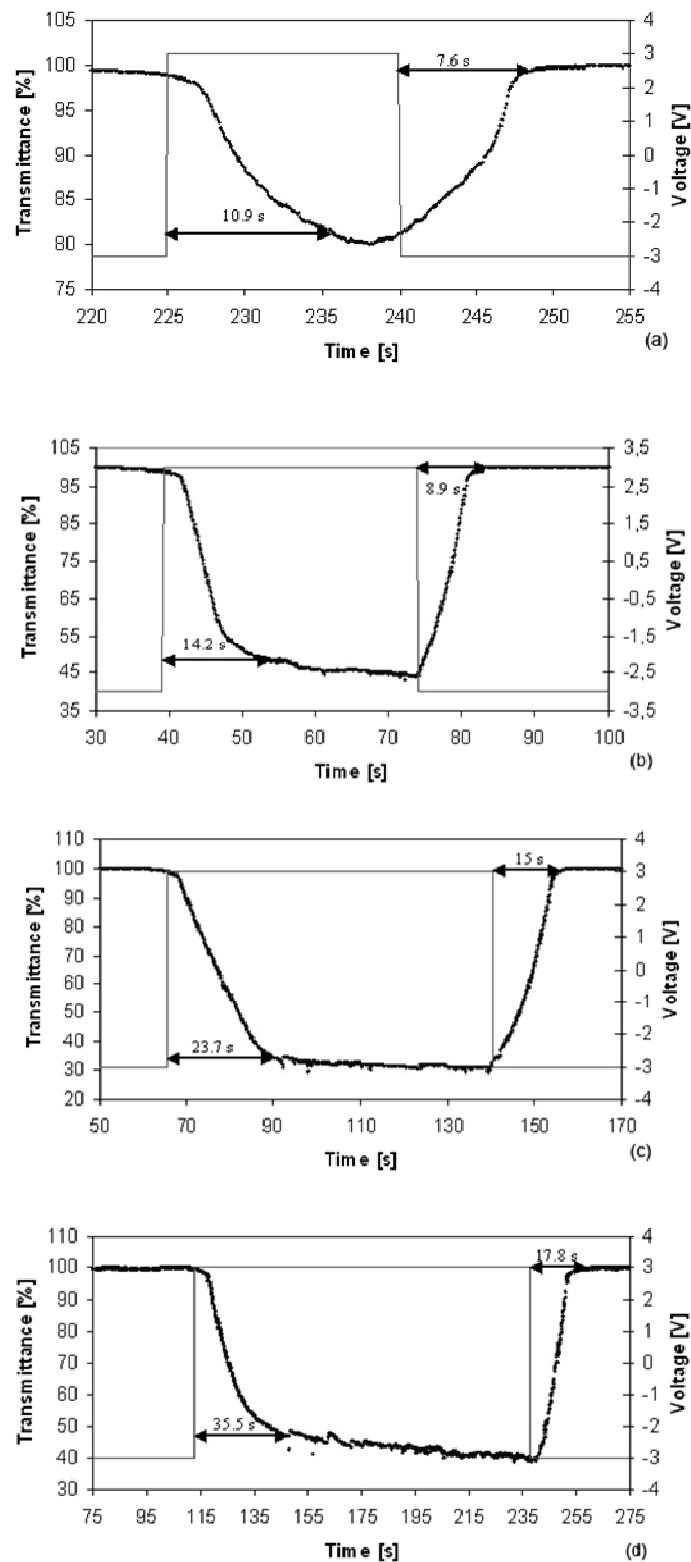


Fig. 3. : Time response of the transmittance at white light for chemically deposited Ni oxide films grown for 10 min (a), 15 min (b), 20 min (c) and 60 min (d).

The pulse potential cycling test provides information on the kinetics related to coloring-bleaching process. Fig. 3 presents one cycle of coloring – bleaching process during the pulse potential cycling test between -3 V and +3 V of the nickel oxide films grown for 10 min (a), 15 min (b), 20 min (c) and 60 min (d). The coloring and bleaching times (time to reach fully colored and fully bleached states respectively) [1] were estimated from Fig. 3.

Fig 4 shows the coloring and bleaching response time for white light as a function of growth time. In order to quantitatively compare the electrochromic response time between all samples, the normalized transmittance curve was used i.e. the transmittance the FTO/glass with the electrolyte and the cell window was assumed to be 100%. From the normalized transmittance curve, the electrochromic response time was calculated as time to reach the fully change in the transmittance. The coloring response time was higher than the bleaching response time. It could be explained with the lower conductivity of Ni(OH)₂ (bleached state) than that of the NiOOH (colored state) [12, 15].

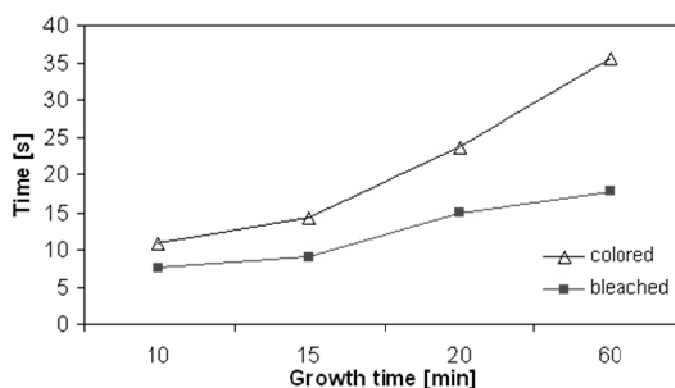


Fig. 4. Electrochromic response time for white light as a function of growth time during the coloring and bleaching process, as calculated from the normalized transmittance curves

Fig. 5 presents the optical density difference ($\Delta OD = \ln(T_{\text{bleached}}/T_{\text{colored}})$), and coloration efficiency for white light ($CE = A \Delta OD / Q$) as a function of growth time, where Q is the charge used during the coloring process calculated by the applied current and the time of its application, and A is the active area of the electrochromic film. The ΔOD gradually increased with growth time. Exception is the thickest film where decreasing in ΔOD was observed which is due to the lower difference between the transmittance in the bleached and the colored states of the film. Chemically deposited nickel oxide films studied in this work had a good coloration efficiency compared with the films obtained by the other methods [1, 12, 14]. The coloration efficiency (CE) tended to have low value for the thick samples as presented in Fig. 4. Although CE is one of the most important properties for improving electrochromic devices, the exact mechanism with respect to CE is not clear yet.

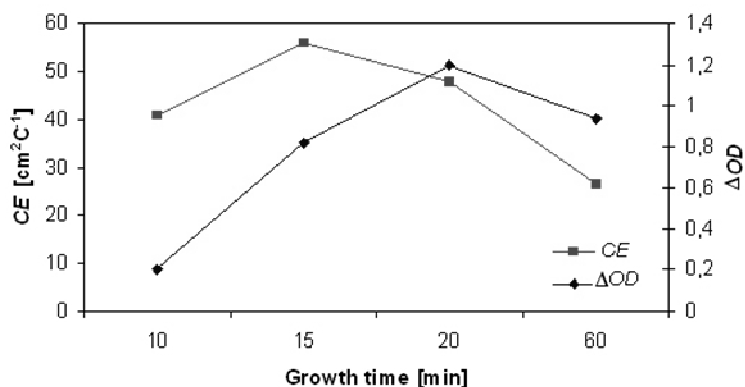


Fig. 5. Optical density difference (ΔOD), and coloration efficiency (CE) for white light as a function of growth time.

4. CONCLUSIONS

Nickel oxide films were prepared by chemical deposition technique onto fluorine doped tin oxide (FTO) coated glass substrates. The difference in the thickness of the films was obtained by adjusting of growth time. All obtained films reveal electrochromism changing color from transparent to dark brown. With increasing growth time, the change in transmittance ΔT or the optical density difference ΔOD was increased except for the thickest film because the maximum bleached transmittance decreased for the thick samples. Those films have good coloration efficiency (CE) compared with the films obtained by other methods of deposition. The CE value decreased for the thickest film and the reasons for this are not presently clear. The electrochromic response time increased with increasing growth time. A higher coloring response time than bleaching response time was observed which could be explained by the difference in the conductivity of the bleached state $[\text{Ni}(\text{OH})_2]$ and the colored state (NiOOH) of the film. The data herein will be potentially useful for designing complementary electrochromic devices with respect to film thickness.

5. REFERENCES

- [1] C.G. Granqvist, "Handbook of Inorganic Electrochromic Materials" Elsevier, Amsterdam (1995), reprinted 2002
- [2] P.M.S. Monk, R.J. Mortimer, D.R. Rosseinsky, "Electrochromism: fundamentals and applications", VCH Verlagsgesellschaft mbH d-69451 Weinheim, Germany (1995)
- [3] A. Azens, G. Vaivars, M. Veszelei, I. Kullman, C. G. Granqvist, J. Appl. Phys. **89** (2001) 7885
- [4] K.S. Ahn, Y.C. Nah, Y.E. Sung, J. Vac. Sci. Technol. A **20** (4), (2002) 1468
- [5] D. D. Ragan, P. Svedlindh, C. G. Granqvist, Sol. Energy Mater. Sol. Cells **54** (1998) 247
- [6] M. Kitao, K. Izawa, S. Yamada, Sol. Energy Mater. Sol. Cells **39** (1995) 115

- [7] T. Maruyama, S. Arai, Sol. Energy Mater. Sol. Cells **30** (1993) 257
[8] J. Arakaki, R. Reyes, M. Horn, W. Estrada, Sol. Energy Mater. Sol. Cells **37** (1995) 33
[9] Z. Yiao, M. Wu, Z. Qin, H. Xu, Nanotechnology **14** (2003) 458
[10] L. C. Chen, K.C. Ho, Electrochim. Acta **46** (2001) 2151
[11] S. Yamada, T. Yoshioka, M. Miyashita, K. Urabe, M. Kitao, J. Appl. Phys. **63** (1988) 2116
[12] K. S. Ahn, Y. C. Nah, Y. E. Sung, J. Vac. Sci. Technol. **A 20 (4)** (2002) 1468
[13] R. Cinnsealach, G. Boschloo, S. Nagaraja Rao, D. Fitzmarice, Sol. Energy Mater. Sol. Cells **55** (1998) 215
[14] J. Velevska, M. Ristova, Sol. Energy Mater. Sol. Cells **73** (2002) 131
[15] A. Gorenstein, F. Dechker, W. Estrada, C. Esteves, A. Andersson, S. Passerini, S. Pantaloni, B. Scrosati, J. Electroanal. Chem. **277** (1990) 277

ЗАВИСНОСТ ОД ДЕБЕЛИНАТА И ЕЛЕКТРОХРОМНИ КАРАКТЕРИСТИКИ НА НИКЕЛ ОКСИДНИ ФИЛМОВИ ПРИГОТВЕНИ СО ХЕМИСКА ДЕПОЗИЦИЈА

Ј. Велевска¹, М. Пецовска - Ѓорѓевиќ¹, М. Најдоски², Н. Стојанов¹

¹Институт за физика, Природно-математички факултет,
П. Фах 162, 1001 Скопје, Macedonia

²Институт за хемија, Природно-математички факултет,
П. Фах 162, 1001 Скопје, Macedonia

Апстракт. Зависноста од дебелината и електрохромните карактеристики на никел оксидни филмови подготвени со хемиска депозиција беа истражувани како функција од времето на растење на филмот со помош на *in situ* мерења на трансмисијата. За таа цел беше конструирана електрохромна тест ќелија во која филмовите од никел оксид беа употребени како работна електрода а стакло обложено со алуминиум оксид допингуван со флуор (FTO) беше употребено како спротивна електрода во алкална средина 0.1 M NaOH воден раствор. Добиените филмови покажуваа аноден електрохромизам менувајќи ја бојата од безбојна до темно кафена. Во овој труд е испитана зависноста на разликата во оптичката густина (ΔOD), ефикасноста на обојување (CE) и времето на обојување и обезбојување на филмовите во зависност од нивната дебелина.