

ELECTROCHROMIC BEHAVIOR OF NiO THIN FILMS DEPOSITED BY E-BEAM EVAPORATION AT ROOM TEMPERATURE

S. Pereira, A. Gonçalves, N. Correia, J. Pinto, L. Pereira, R. Martins and E. Fortunato*



* sp@uninova.pt

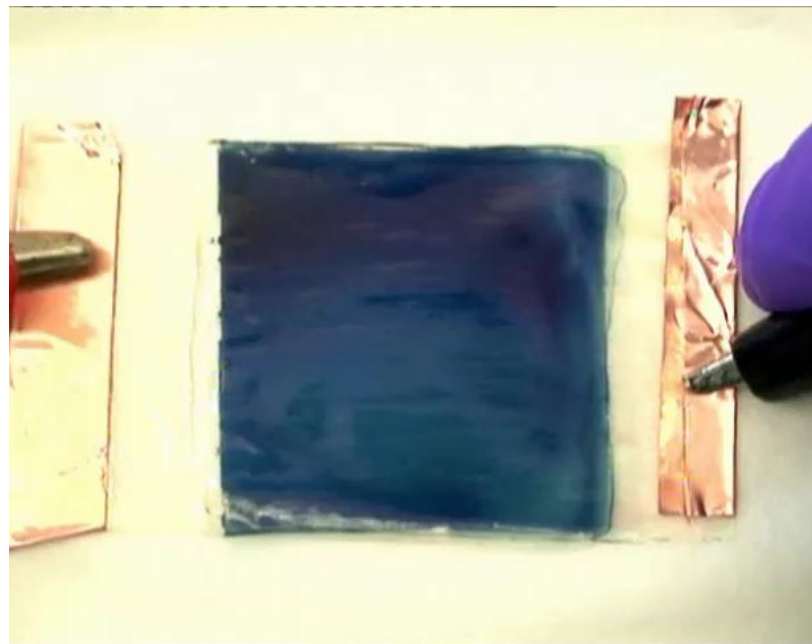
OUTLINE

- ❑ Introduction
- ❑ Experimental details
- ❑ Results and discussion
- ❑ Conclusions and future perspectives



INTRODUCTION

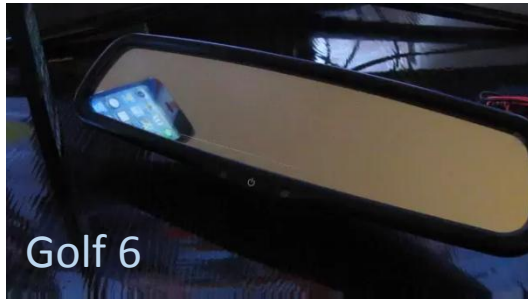
ELECTROCHROMISM



INTRODUCTION – HOW DOES AN EC DEVICE WORKS?



INTRODUCTION – APPLICATIONS



<http://www.youtube.com/watch?v=NGWznDgH2fw>



Avendano et al, Materials Science and Engineering B, 2007



http://www.youtube.com/results?search_query=boeing%20787%20windows&sm=3



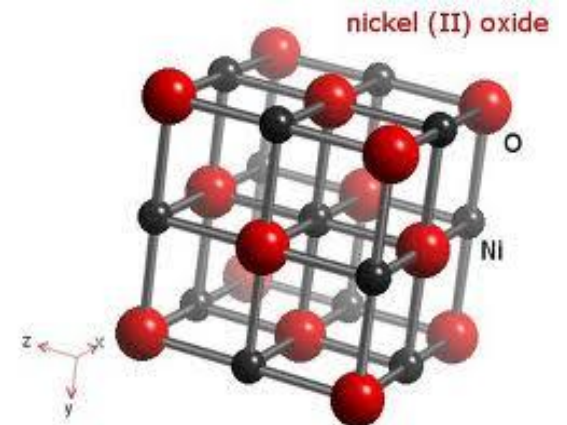
<http://sageglass.com/sageglass/>

INTRODUCTION – NICKEL OXIDE (NiO)

Good cyclic reversibility $\cong 8$ s

High coloration efficiency $\cong 40 \text{ cm}^2\text{C}^{-1}$

Good durability > 100 cycles



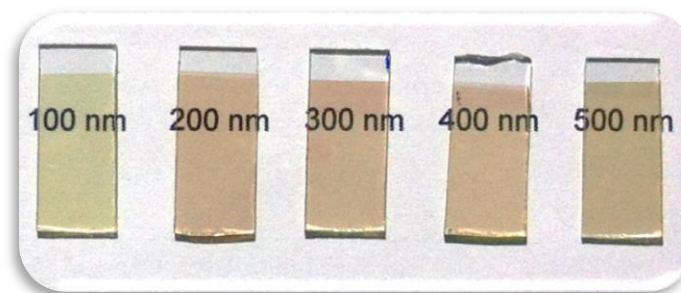
EXPERIMENTAL DETAILS



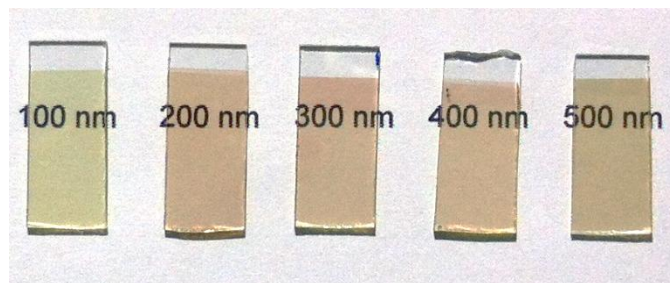
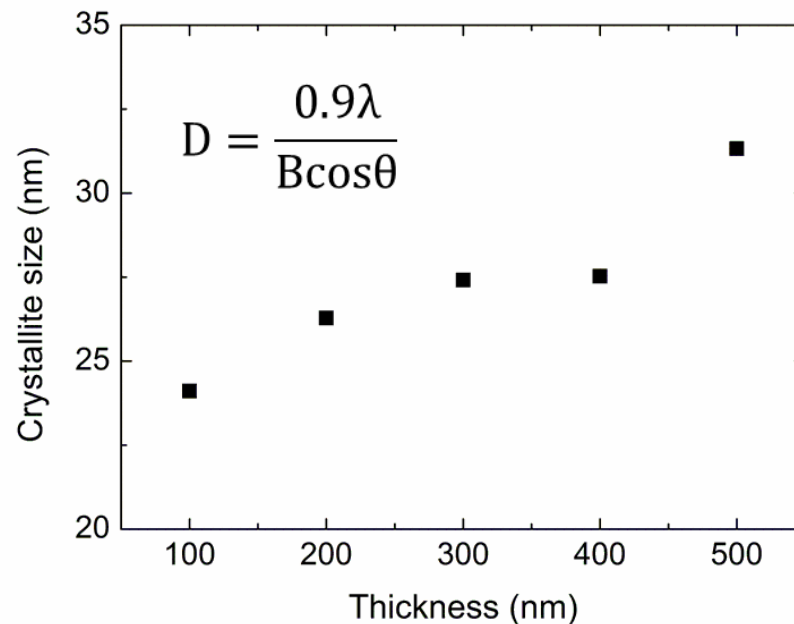
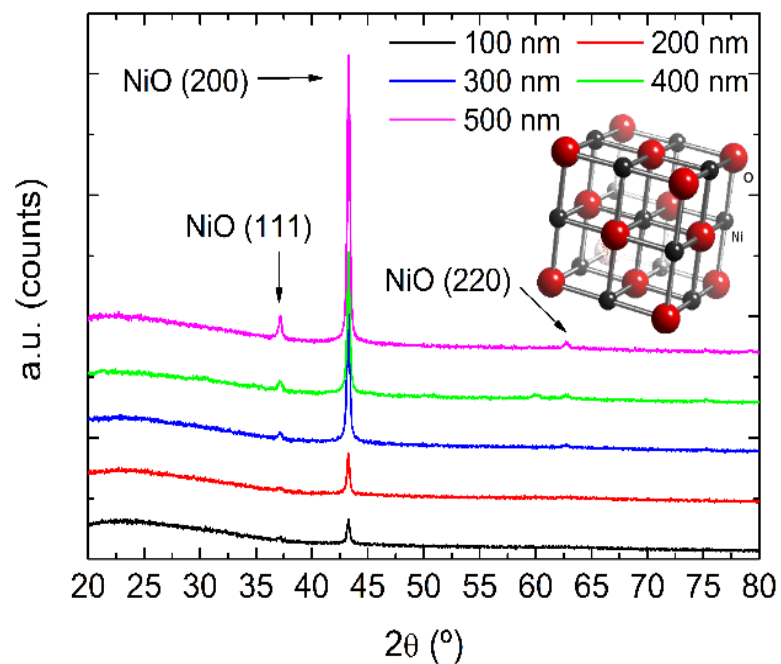
SCM pellets, 3-6 mm, 99.99 purity



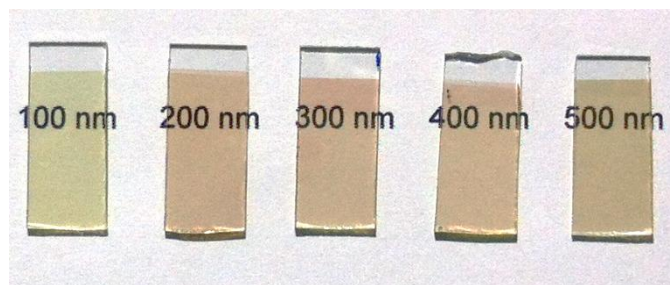
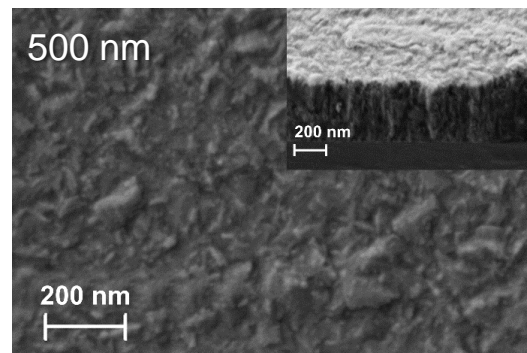
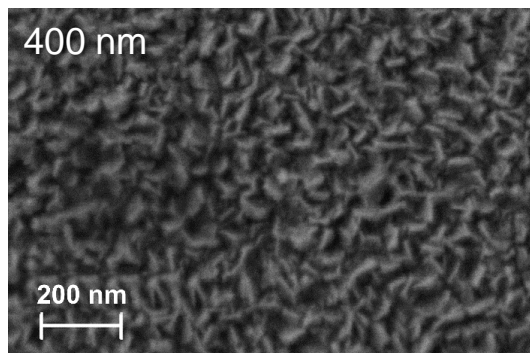
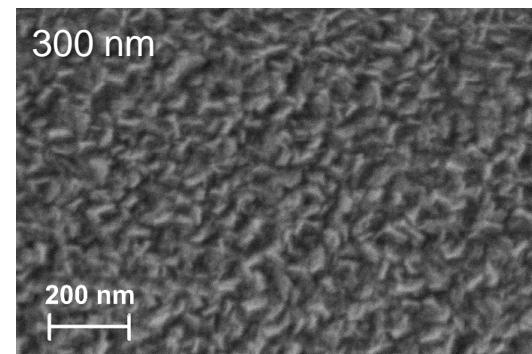
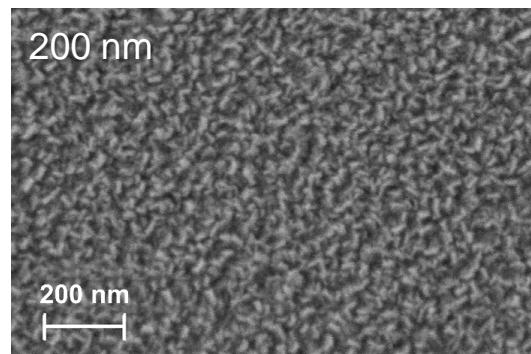
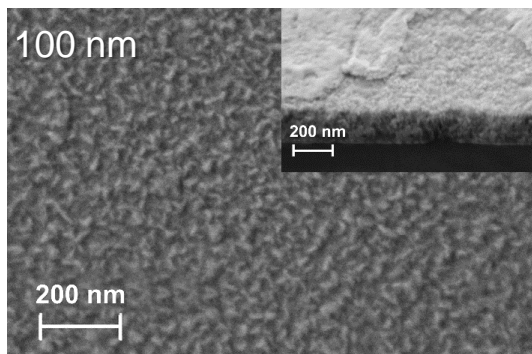
Evaporation rate: 0.3-0.5 Å/s
Applied current: 5-30 mA



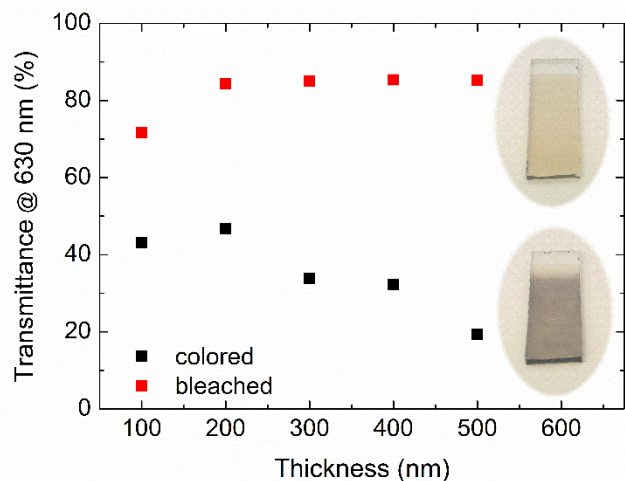
RESULTS AND DISCUSSION - XRD



RESULTS AND DISCUSSION - SEM



RESULTS AND DISCUSSION – OPTICAL PROPERTIES



Electrolyte : 0.5 M LiClO₄-PC

Applied voltage : ± 2 V

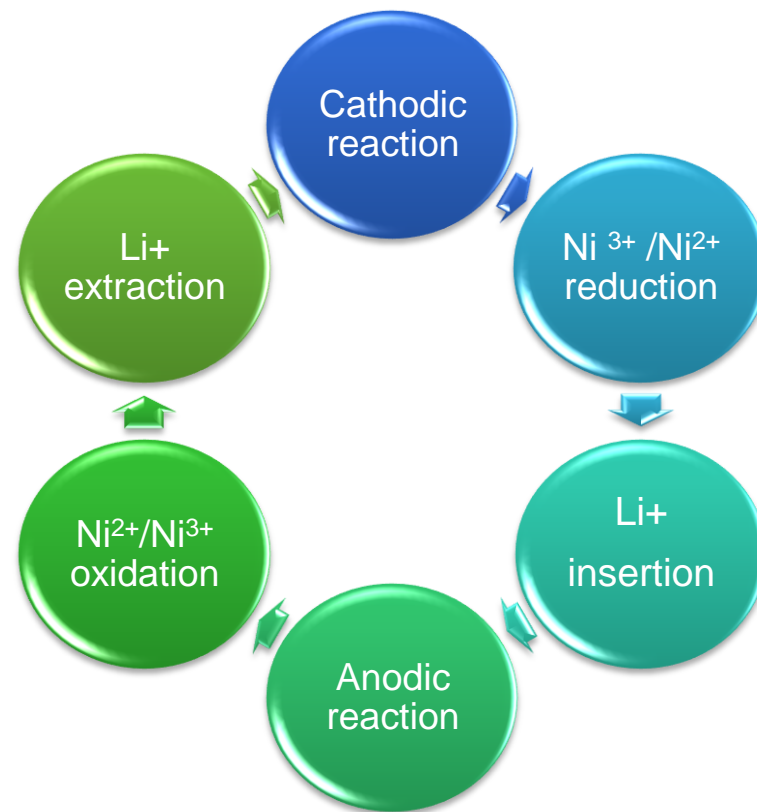
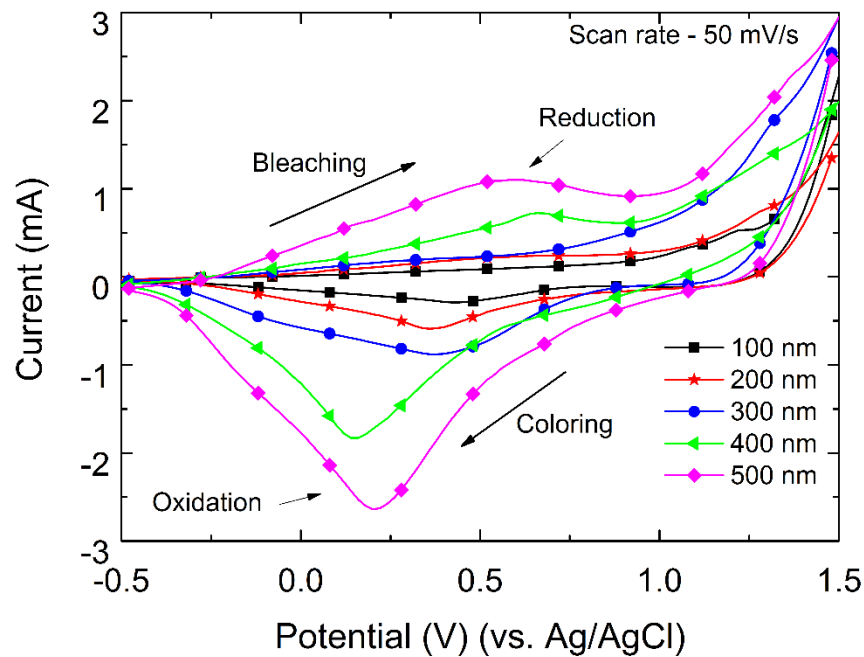
Active area : 1 cm²

$$\Delta OD = \log \left(\frac{T_b}{T_c} \right)_{\lambda=630\text{nm}}$$

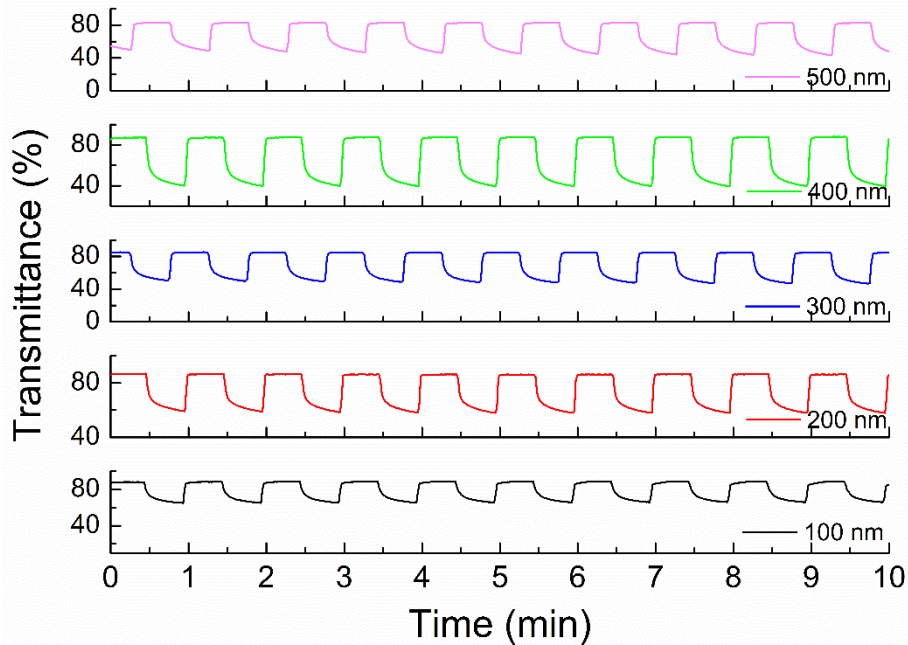
$$CE = \left(\frac{\Delta OD}{Q_i} \right)_{\lambda=630\text{nm}}$$

Nomenclature	Optical Density (ΔOD)	Color Efficiency (cm ² C ⁻¹)
100 nm	0.22	31
200 nm	0.26	33
300 nm	0.40	35
400 nm	0.42	54
500 nm	0.64	55

RESULTS AND DISCUSSION - CVs



RESULTS AND DISCUSSION – REVERSIBILITY AND RESPONSE TIMES



Samples 400 e 500 nm > 200 cycles

Samples 300 nm = 130 cycles

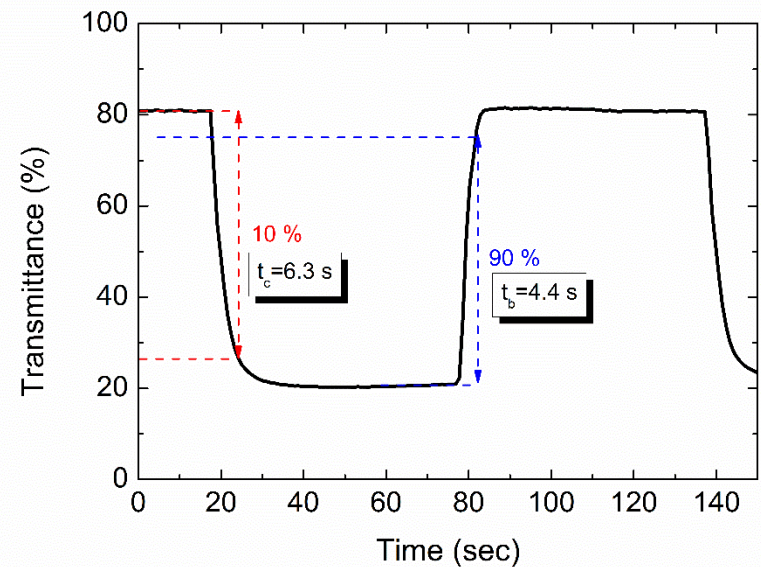
Samples 100 e 200 nm = 100 cycles

$t_{\text{colored}} 100 \text{ nm} = 3.2 \text{ s}$

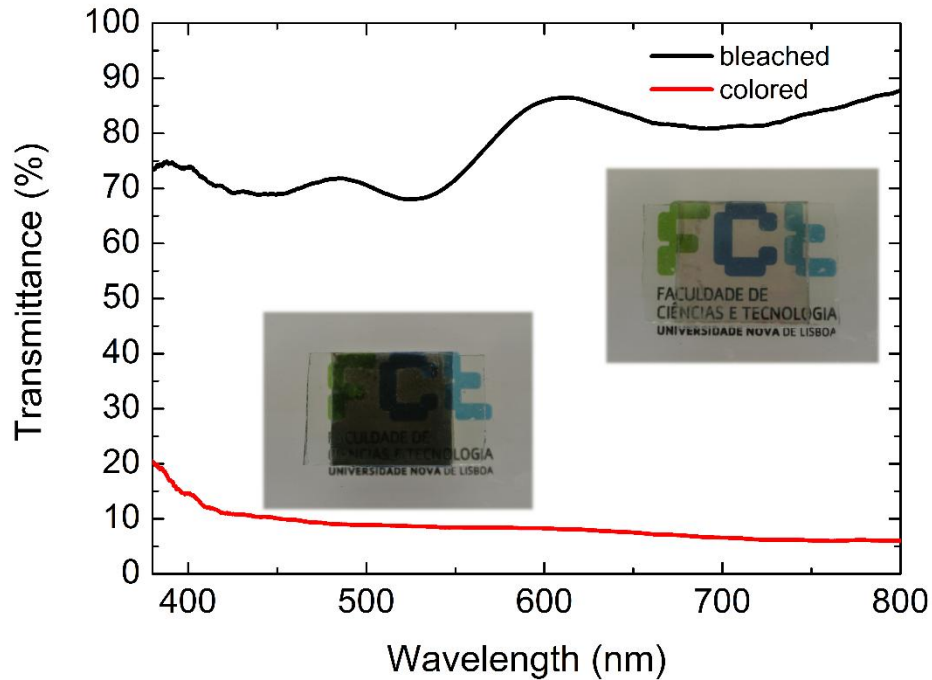
$t_{\text{colored}} 500 \text{ nm} = 6.3 \text{ s}$

$t_{\text{bleached}} 100 \text{ nm} = 1.0 \text{ s}$

$t_{\text{bleached}} 500 \text{ nm} = 4.4 \text{ s}$

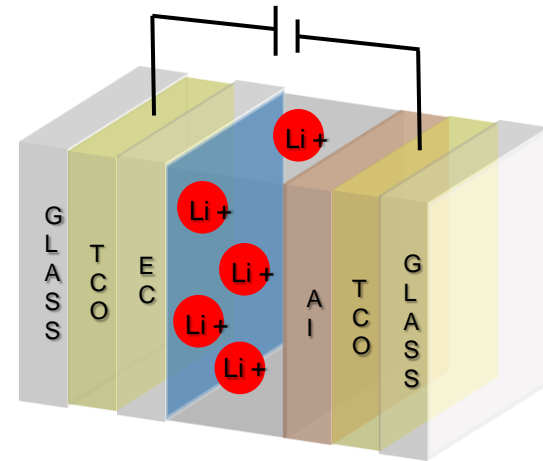


RESULTS AND DISCUSSION - PROTOTYPE



Applied voltage = ± 2 V

$$\Delta T_{630 \text{ nm}} = 77\%$$



ITO/ WO_3 /LiClO₄-PC/NiO/ITO

CONCLUSIONS AND FUTURE PERSPECTIVES

- Structure and morphology → policrystalline with cubic fase
→ crystallite size: 20 – 40 nm

NO ANNEALING

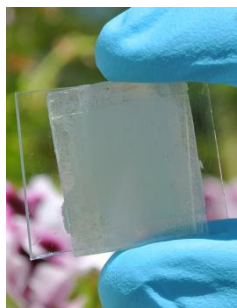
- Electrochromic behavior

	ΔT (%)	CE (cm^2C^{-1})	t_{col} (s)	t_{blea} (s)	Reversibility
100 nm	29	31	3.2	1.0	100
200 nm	38	33	3.9	1.7	100
300 nm	51	35	4.8	2.9	130
400 nm	53	54	5.7	3.8	> 200
500 nm	66	55	6.3	4.4	> 200

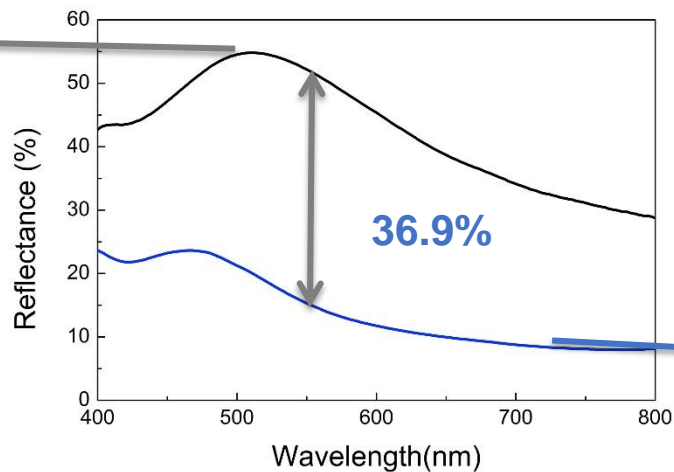
- ITO/ WO_3 / LiClO_4 -PC/ NiO /ITO → $\Delta T = 77\%$

CONCLUSION AND FUTURE PERSPECTIVES

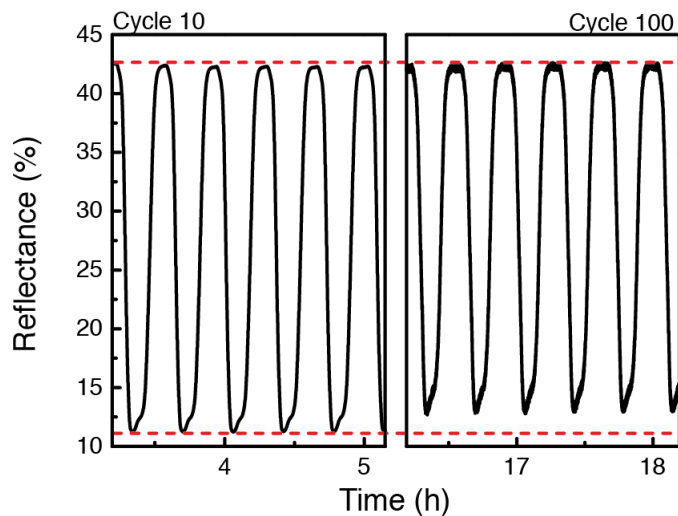
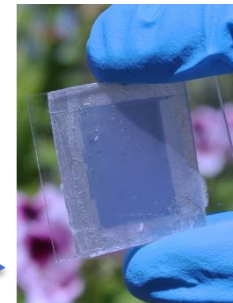
- Different electrolytes and flexible substrates



Bleached State



Colored State



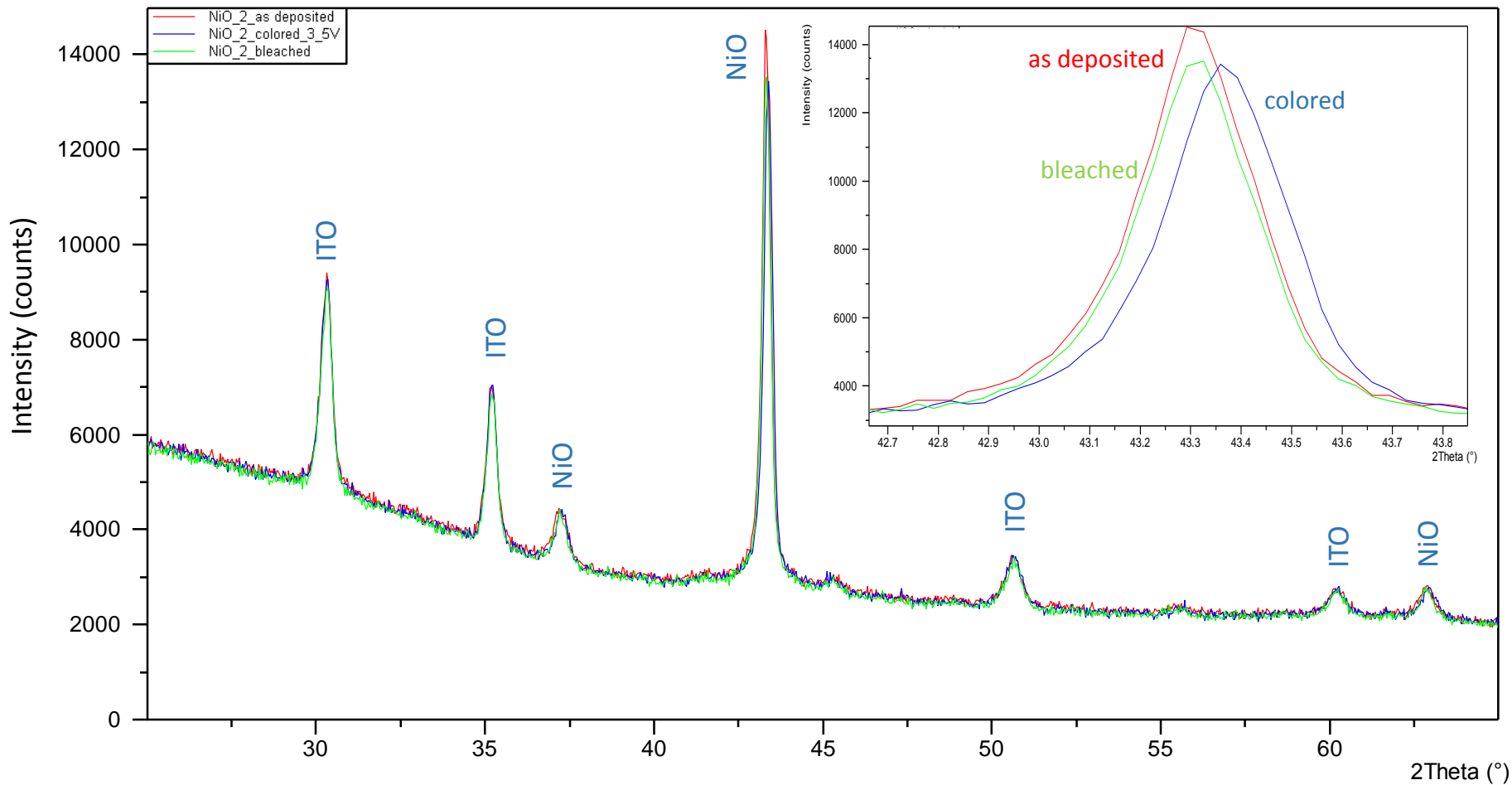
Flexible Device - Proof-of-Concept



PET / ITO / WO₃ / Cellulose Solid Electrolyte / NIO / ITO / PET

CONCLUSION AND FUTURE PERSPECTIVES

□ In-situ XRD – Lithiation of Li ions



CONCLUSION AND FUTURE PERSPECTIVES

ELECTROCHROMIC DEVICE INCLUDING A Li^+ -BASED HYBRID ELECTROLYTE DOPED WITH AN IONIC LIQUID

Maria C. Gonçalves¹, Mariana Fernandes¹, Sónia Pereira², Elvira Fortunato², Rosa Rego¹ and Verónica de Zea Bermudez¹

¹ Departamento de Química e CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal

² CENIMAT, CENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
E-mail: cristina@utad.pt

Amorphous di-urethane cross-linked poly(oxyethylene) (POE)/siloxane hybrid materials, designated as *di-urethanesils* (represented as d-Ut(600), where 600 indicates the average molecular weight of the polymer segment) doped with lithium triflate (LiCF_3SO_3) with compositions $\infty > n \geq 1$ (where n is the molar ratio of $(\text{OCH}_2\text{CH}_2)$ repeat units per Li^+) were reported by our group [1]. The host hybrid matrix d-Ut(600) incorporates POE chains with approximately 13 $(\text{OCH}_2\text{CH}_2)$ repeat units. The sample with $n = 1$ (denoted as $\text{d-Ut}(600)_1\text{LiCF}_3\text{SO}_3$) exhibits the highest conductivity of the system at room temperature (approximately $7.4 \times 10^{-5} \text{ Scm}^{-1}$) and displays excellent redox stability.

In the present work we have doped $\text{d-Ut}(600)_1\text{LiCF}_3\text{SO}_3$ with a commercial ionic liquid. This electrolyte was used in a prototype electrochromic device (ECD) with the glass/ITO/ WO_3 /electrolyte/NiO/ITO/glass configuration [2]. The average optical transmittance, color contrast, optical density and device response time associated with the coloring/bleaching process have been determined. The time stability of the ECD has been tested by chronoamperometry measurements. The bleaching/coloration kinetics have been quantified and the coloring efficiency has been calculated.





IF: 4.630

Electrochromic behavior of NiO thin films deposited by e-beam evaporation at room temperature



Sónia Pereira*, Alexandra Gonçalves, Nuno Correia, Joana Pinto, Luís Pereira, Rodrigo Martins, Elvira Fortunato*

CENIMAT/3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, FCT Universidade Nova de Lisboa and CEMDP-UNINOVA, Campus de Caporita, 2829-516 Caporita, Portugal

ARTICLE INFO

Article history:

Received 20 September 2012

Received in revised form

2 August 2013

Accepted 22 August 2013

Available online 16 September 2013

Keywords:

Nickel oxide

Electrochromic devices

Thermal evaporation

Chromogenic materials

ABSTRACT

In this work we report the role of thickness on electrochromic behavior of nickel oxide (NiO) films deposited by e-beam evaporation at room temperature on ITO-coated glass. The structure and morphology of films with thicknesses between 100 and 500 nm were analyzed and then correlated with electrochemical response and transmittance modulation when immersed in 0.5 M LiClO₄-PC electrolyte. The NiO exhibits an anodic coloration, reaching for the thickest film a transmittance modulation of 86% between colored and bleached state, at 630 nm, with a color efficiency of 35 cm² C⁻¹. Very fast switch between states was obtained, where coloration and bleaching times are 3.6 s cm⁻² and 1.4 s cm⁻², respectively.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Electrochromic (EC) materials are able to change their optical properties by the application of an electric potential [1]. Their optical absorption can be reversibly modified through ionic (or proton) insertion and charge compensating electrons allowing for adjustable color modulation and making possible its application in electrochromic devices. When considering inorganic materials this phenomenon can be observed in many oxides of transition metal elements, where two different types of coloration may occur depending on whether the material darkens under ion insertion (cathodic coloration) or ion extraction (anodic coloration) [2–4]. Tungsten trioxide (WO₃), the most studied electrochromic material [5,6] presents cathodic coloration so, in order to improve the optical modulation of an electrochromic window, it is relevant to study materials that present complementary coloration (anodic coloration) [7,8]. One good candidate is nickel oxide (NiO) that is a low cost material allowing for good cyclic reversibility, high coloration efficiency and good durability [9–11]. NiO presents a brownish color on the colored state and it is highly transparent on the bleached state [12,13]. If both NiO and WO₃ are combined in the same electrochromic device it is possible to improve the transmittance modulation making them very attractive for applications on smart windows or displays to be used in automobiles,

buildings or airplanes [14–16]. These devices can even be incorporated in thermal sensitive substrates (e.g. paper) due to the low temperature deposition process required [17,18].

There are several reports on NiO thin films for electrochromic applications obtained by different physical or chemical deposition techniques. Among the physical routes known, sputtering and resistive thermal evaporation both have been often used [3,19,20]. In most of these works usually NiO requires a post-deposition annealing treatment [9,11,21,22], being known few reports on non-annealed NiO films aiming their use as electrochromic material [20,23]. In this work we report the electrochromic behavior of evaporated NiO layers without any intentional substrate heating or post-deposition treatment. Moreover, we have focused the present work on the role of the thickness of NiO films on the morphology, structure and electrochromic properties. The films were tested on a nonaqueous solution of 0.5 M LiClO₄-PC as this electrolyte is compatible with both WO₃ and NiO turning possible in future work the development of electrochromic windows with a ITO/WO₃/LiClO₄-PC electrolyte/NiO/ITO structure. Also, due to the small size of a Li⁺ containing electrolyte the insertion/extraction kinetics is faster than that of OH⁻ ions [24].

2. Experimental

NiO thin films were deposited on indium tin oxide-coated glass (ITO from Xih Yan Technology with a sheet resistance of 10 Ω/□) and a transmittance in the visible region of 85% by e-beam

* Corresponding authors. Tel.: +351 212948562; fax: +351 212948558.
E-mail addresses: sp@uninova.pt (S. Pereira), emf@ct.unl.pt (E. Fortunato).

ACKNOWLEDGMENTS



FCT

Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR



Grant no. 258203

Electra

PTDC/CTM/099124



4th Jornadas of CENIMAT/I3N – 23rd June 2014

THANK YOU!