

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**MAGNETRON SPUTTER DEPOSITION
OF METAL-OXIDE THIN FILM LAYERS
FOR ELECTROCHROMIC DEVICE
APPLICATIONS**

by
Jose Enrique MARTINEZ MEDINA

November, 2020
İZMİR

MAGNETRON SPUTTER DEPOSITION OF METAL-OXIDE THIN FILM LAYERS FOR ELECTROCHROMIC DEVICE APPLICATIONS

**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University in
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**by
Jose Enrique MARTINEZ MEDINA**

November, 2020

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M.Sc THESIS EXAMINATION RESULT FORM

We have read this thesis entitled "MAGNETRON SPUTTER DEPOSITION OF METAL-OXIDE THIN FILM LAYERS FOR ELECTROCHROMIC DEVICE APPLICATIONS" completed by JOSE ENRIQUE MARTINEZ MEDINA under supervision of PROF. DR. ELİF ŞAHİN IŞGIN and PROF. DR. GÜLNUR AYGÜN and we certify that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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Jose Enrique MARTINEZ MEDINA

MAGNETRON SPUTTER DEPOSITION OF METAL-OXIDE THIN FILM LAYERS FOR ELECTROCHROMIC DEVICE APPLICATIONS

ABSTRACT

Electrochromism is the property of certain materials which involves a change from a bleaching state to a colored state as effect either by the action of an electrical voltage or current. Electrochromic devices (ECD) are formed by materials that are capable of continuously and reversibly modulating their color, usually from a bleaching state to a colored one, with the application of a small electric current. Among this electrochromic materials, WO_3 and NiO_x metal oxides are the dominant among the electrochromic metal oxides. The applied electric current induces in them a reaction of reduction (gain of electrons) or oxidation (loss of electrons) that modifies the range of energies in which the compound interacts with visible light.

In this work WO_3 and NiO_x were deposited onto ITO coated glass by reactive DC magnetron sputtering in Ar/O_2 mixing gas at room temperature. For the deposition process was employed off-axis sputtering method in which the substrate is positioned out of the high-energy particles. The electrochemical properties of the WO_3 and NiO_x series were measured by using conventional three-electrode configuration in 1 M LiClO_4 -PC electrolyte. Then with the aim to test the performance of the electrochromic metal oxide films, a five-layer battery-like structure ECD ($\text{ITO}/\text{WO}_3/\text{electrolyte}/\text{NiO}_x/\text{ITO}$) was assembled with an Li^+ based liquid electrolyte. The results confirm that off-axis magnetron sputtering provides good feasibility to deposit metal oxide thin films with a good electrochromic performance.

Keywords: Electrochromic materials, optical modulation, electrochromic devices, thin film

ELEKTROKROMİK CİHAZ UYGULAMALARI İÇİN METAL OKSİT İNCE FİLM KATMANLARININ MİKNOTISSAL SAÇTIRMA TEKNİĞİYLE KAPLANMASI

ÖZ

Elektrokromizm, bir elektrik voltajının veya akımın etkisiyle ağartma durumundan renkli duruma olan değişimi içeren belirli malzemelerin özelliğidir. Elektrokromik cihazlar, küçük bir elektrik akımının uygulanmasıyla rengini, genellikle ağartma durumundan renkli duruma, devamlı ve tersine çevrilebilir olarak değiştirebilen malzemelerden oluşur. Bu elektrokromik malzemeler arasında WO_3 ve NiO_x metal oksitler, elektrokromik metal oksitler arasında baskındır. Uygulanan elektrik akımı, içlerinde bileşiğin görünür ışıkla etkileşime girdiği enerji aralığını değiştiren indirgenme (elektron kazancı) veya yükseltgenme (elektron kaybı) reaksiyonuna neden olur.

Bu çalışmada, WO_3 ve NiO_x , oda sıcaklığında Ar/O_2 gaz karışımı varlığında reaktif DC magnetron püskürtme yöntemi ile ITO kaplı cam üzerinde büyütüldü. Büyütülme için, substratın yüksek enerjili parçacıkların dışına konumlandırıldığı eksen dışı püskürtme yöntemi uygulandı. WO_3 ve NiO_x serilerinin elektrokimyasal özellikleri, geleneksel üç elektrot konfigürasyonu kullanılarak 1 M $LiClO_4$ -PC elektrolit içinde ölçüldü. Daha sonra, elektrokromik metal oksit filmlerin performansını test etmek amacıyla, beş katmanlı pil benzeri yapısı olan elektrokromik cihazlar (ITO/WO_3 /electrolyte/ NiO_x /ITO), Li bazlı sıvı elektrolit ile monte edildi.

Anahtar kelimeler: Elektrokromik malzemeler, optik modülasyon, elektrokromik cihazlar, ince film

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CHAPTER ONE

INTRODUCTION

Over the past decades electrochromic devices (ECD) have been investigated due to their modulating optical properties (transmittance, reflectance, and absorption) reversibly by applying a voltage. These ECDs have a wide range of applications in modern technology such as electrochromic supercapacitors, optical information displays, switchable mirrors, EC windows that efficiently modulate the transmission of light and heat, etc (Niklasson & Granqvist, 2007; Chen, P. et al., 2020; L. Liu et al., 2019).

Among a wide variety of electrochromic (EC) materials such as conductive polymer thin films and small organic molecules, metal oxides have crucial role in ECD applications for modulating optical properties reversibly and persistently, through the application of electrical current or voltage (Granqvist et al., 2019). In the group of these EC oxides, exist "cathodic" and "anodic" coloring: Those that change from a transparent to a colored state under insertion of M^+ ions are called cathodic and those that change from a colored to transparent state under extraction of M^+ ions are named anodic. Tungsten oxide (WO_3) and Nickel Oxide (NiO_x) are the most widely cathodic and anodic coloring EC oxides respectively (Chen, P. et al., 2020; Granqvist, 2019).

A typical electrochromic device has a structure and behavior similar to a battery which consist of 5 laminated layers, this is when a Li^+ ion electrolyte is employed, the ECD become a battery sandwiched by transparent electrodes. For the configuration in this ECD, optical modulation arise when Li^+ are transported between the cathodic coloring WO_3 and anodic coloring NiO_x followed by charge-balancing injection/ejection of electrons and ions under an applied bias to the ITO transparent electrodes (He et al., 2018; Kraft, 2018). The optical transmission of the electrochromic device can be repeatedly reversed by exchange of charges and electrons. Also the electrochromic properties should remain constant without any defect arising inside the device. To achieve this, the intercalation and extraction of Li^+ in the electrochromic layers is influenced principally by surface, structure, porosity and composition (Dong et al., 2018; Niklasson & Granqvist, 2007; He et al., 2018).

CHAPTER TWO

LITERATURE SURVEY

2.1 Chromogenics

Chromogenics (derivated from the Greek expression ‘chromo’ which means color) is refered to the study of materials with the property of reversible modification in their optical characteristics as function of environmental conditions or under an applied stimulus such as mechanical, thermal, optical or electrical (Ashrit, 2017; Nunes et al., 2019). This kind of reversible optical properties can be applied to an extensive variety of chromogenic device technologies, which can be classified into different categories, depending from the energy source or stimulus which induces the change in their optical properties such as thermochromic (depending on temperature), magnetochromic (depending on applied magnetic field), photochromic (depending on ultraviolet irradiation), biochromic (depending on pathogens presence), electrochromic (depending on electrical voltage or charge), etc., either by themselves or in combinations, in which light control is needed or depending on the specific applications of automated smart systems (Bamfield & Hutchings, 2010; Nunes et al., 2019). The investigation of new chromogenic materials has been expanding over the past few years, the evolution of these smart materials along history is displayed in Figure 2.1.

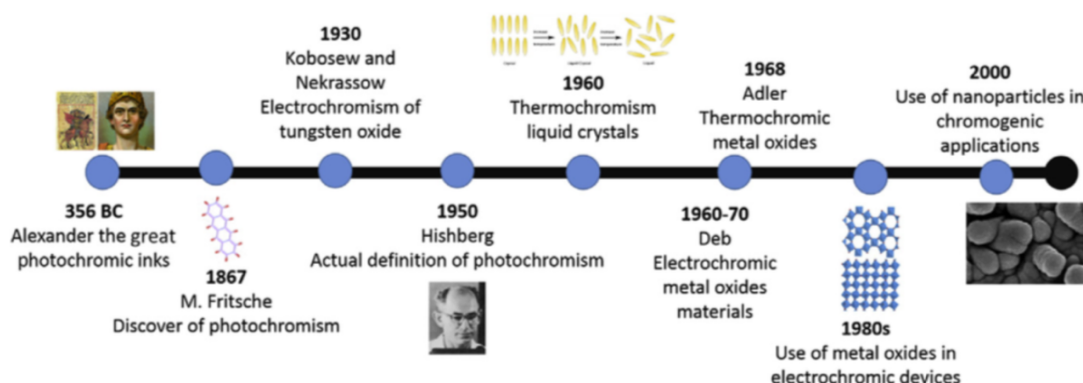


Figure 2.1 Development of chromogenic materials along history (Nunes et al., 2019)

2.2 Electrochromism and Electrochromic Materials

Electrochromism is an optical phenomenon of reversible coloration change, conventionally from a non color or transparent state to a colored one and inversely, derivated from the electrochemical oxidation/reduction reactions in these "electrochromic materials" (EC). These materials, also known as "electrochromes" are characterized by their optical property of reversible color change caused by applying an electric potential which involves electrochemical redox reaction into the electrochromic material (Granqvist et al., 2018; Dong et al., 2018). For instance, electrochromes that are coloured in their oxidized states are known as anodically colouring and the ones that are coloured in their reduced states are referred to as cathodically colouring electrochromes. The EC materials have gained a great attention because of their extraordinary diversity of applications as for example, self-dimming rear mirrors, information displays and electrochromic e-skins, smart windows for energy efficient buildings, electrochromic supercapacitors and electrochromic batteries and so on (Wu et al., 2018). These make the EC materials the most extensively investigated and applied among the different chromogenic materials (Granqvist, 2019).

A wide range of electrochromic materials display high coloration efficiency, such as conjugated conducting polymers, viologens and metal oxides. Thin film metal oxides are the key for the previously mentioned applications since they show large optical modulation, high coloration efficiency (CE), cyclic durability and high ion and electronic conductivity that ensure relatively shorter switching time . There are principally two groups of electrochromic metal oxides for electrochromic applications: the "cathodic" colouring ones under ion intercalation and "anodic" colouring under ion extraction, as is indicated in the Figure 2.2 (Mortimer et al., 2015; Wu et al., 2018). The electrochromic materials should have high coloration efficiency, large optical modulation and cyclic durability. Due to these reasons in this study, WO_3 thin films are investigated as principal electrochromic film and NiO_x as ion storage film that also serves as complementary electrochromic film in the electrochromic device structure.

ELECTROCHROMIC OXIDES:

H																			He
Li	Be																		
Na	Mg																		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	Ac																	

Cathodic coloration

Anodic coloration

Figure 2.2 Periodic system showing the different transition metals capable of forming oxides, giving cathodic and anodic electrochromism (Mortimer et al., 2015)

2.2.1 Tungsten Oxide

Tungsten oxide or tungsten trioxide (WO_3) is a popular d^0 -transition metal-oxide with a wide bandgap n-type semiconductor. The valence band of this metal oxide is constituted by completely filled O $2p$ orbitals and by vacant W $5d$ orbitals in the conduction band (Figure 2.3). The optical band gap of amorphous WO_3 films sputtered reactively from a W target have been reported to be around 3.1 eV and its density depends on the operating pressure and the deposition rate which is around 6.0-6.7 g/cm³ (Niklasson & Granqvist, 2007).

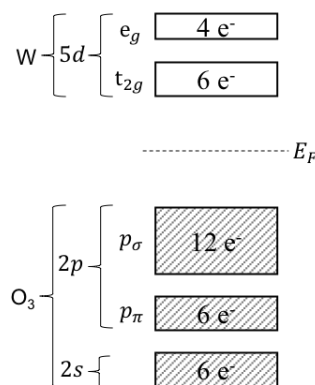


Figure 2.3 Schematic band diagram of WO_3 . Tungsten orbitals are at the top and oxygen orbitals are at the bottom. Filled electronic states are shaded and Fermi level (E_F) is specified by the arrow (Figure adapted from (Niklasson & Granqvist, 2007))

WO₃ is as far the most studied cathodic oxide for electrochromic applications due to its excellent optical modulation, fast switching kinetics, good electrochemical activity and stable cycling life (Chen et al., 2013; J. Yuan et al., 2018). WO₃ modify its optical properties from a transparent state to a deep blue color state reversibly as effect of an applied low voltage bias. The electrochromic mechanism is principally associated to the intercalation/deintercalation of ions and electrons in the film and is expressed according to the following oxidation-reduction equation



where $M = H^+, K^+, Li^+ \text{ or } Na^+$ and x is the molar fraction of ions intercalated into a WO₃ thin film host (G. Yuan et al., 2017; Guo et al., 2018).

It has been observed that the electrochromic coloration property of the crystalline and amorphous WO₃ films is due to ionic insertion and also is well known that crystalline tungsten oxide thin films may have a nonidentical mechanism during the coloration phenomena than those of amorphous WO₃ structure films (Buch et al., 2016; Niklasson & Granqvist, 2007).

The coloration phenomena in crystalline tungsten oxide (c-WO₃) is associated to a Drude-like free electron absorption with highly similarity to the behavior of heavily doped semiconductor with ionized impurities. Crystalline WO₃ thin films exhibit a slow degradation rate upon cycling and good cycling durability because of the dense and well-order in their crystalline structure. Nevertheless, higher energy barriers result in a limited optical modulation range and a slow switching speed (Wen et al., 2015; Lee et al., 2003).

Amorphous WO₃ (a-WO₃) is by far the most popular and most studied EC metal oxide material and is employed in transmittance-modulating electrochromic devices (Wen et al., 2015). Due to the dense crystalline structure of the WO₃ effects the ions to be intercalated through the coloring activity and to be deintercalated through the bleaching activity, a-WO₃ thin films have been extensively investigated because its promising applications in EC windows since a-WO₃ shows better coloration efficiency

and faster response time than crystalline ones (Ding et al., 2018; Yuan et al., 2017; Zhang et al., 2019).

It has been proposed that during the insertion of M^+ ions into the amorphous WO_3 thin film, the compensating electrons become localized at the d states of tungsten, then the W^{6+} states are reduced to W^{5+} ($5d^1$) or W^{4+} ($5d^2$), depending upon the available sites, which induce lattice distortion around the W ion and polarize their surrounding lattice (by short-range interactions) to form small polarons (Kim et al., 2019; Guo et al., 2018). The absorption of incident photons with compatible energy $h\nu$ cause polaron hopping between the two adjacent nonequivalent W sites, as in



where i and j represent the two neighbouring sites according to where the intercalated electrons are located in the W^{5+} sites. The above indicates WO^{5+} states are responsible of the EC behavior in the a- WO_3 thin films (Kim et al., 2019; Niklasson & Granqvist, 2007; Wen et al., 2015). During the coloring process, the number of color centers W^{5+} are increased at the same time that the electrical resistivity and transmission in the visible spectra of the thin film decrease drastically, or in other words, becomes the thin film a dark blue conductor as consequence red light absorption. On the other hand the colored films contain W^{4+} and W^{6+} as well, which varies with the ion intercalation level. During ion extraction process the tungsten oxide lattice valance state returns to its original (or almost original) state (Kim et al., 2019; Guo et al., 2018).

2.2.2 Nickel Oxide

Stoichiometric nickel oxide (NiO) is an insulator whose resistivity values are in the order of $10^{11} \Omega m$ at room temperature (Madhu & Biju, 2014). However, by doping with monovalent ions or by introducing Ni $2p$ vacancies, the resistivity of this material can be decreased, yielding to electrically compensated by electronic holes with cation vacancies p -type semiconductor, as primary defects leading to the origination of Ni^{3+}

states. As consequence of this, non stoichiometric NiO_x has a wide optical band gap between 3.6–4.0 eV (Horak et al., 2017; Qiu et al., 2018). The uppermost section of the valence band in NiO is composed of Ni 3 d states that start at ~ 2 eV under the Fermi level which overlaps with a wide O 2 p band at ~ 4 to 8 eV from the Fermi level; the Ni 3 d and O 2 p states are close to be fully hybridized. The conduction band of NiO is composed of unoccupied Ni 3 d (e_g) states with a mixture of O 2 p states; 4 s and 4 p bands are present at upper energies, as is depicted in Figure 2.4 (Niklasson & Granqvist, 2007).

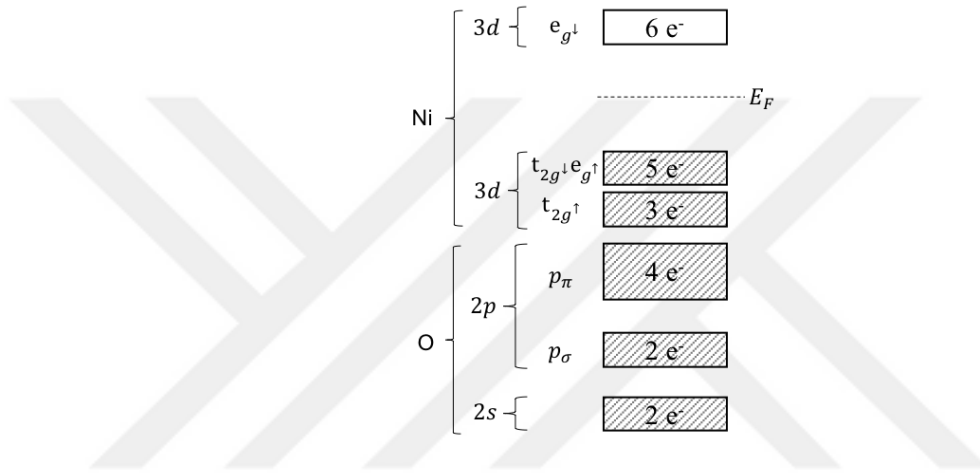
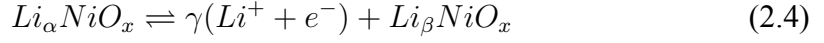
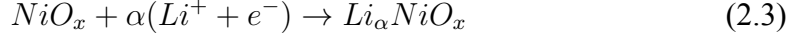


Figure 2.4 Band diagram representation of nickel oxide. Nickel and oxygen orbitals as well as minority and majority of its spin states are specified together with the Fermi level (E_F). The specific number of electrons (e^-) can be fit in the bands. Occupied states are shaded ((Figure adapted from (Niklasson & Granqvist, 2007))).

NiO_x is probalby the most extensively investigated anodic-oxide based EC material because of its high coloration efficiency and low-cost. This anodic coloring material is capable to modify its optical properties from a colored to a bleached state under deintercalation/intercalation of M^+ ions respectively (Qiu et al., 2018). The normally preferred ions due to their higher mobility and size to be the easily inserted/extracted during the coloration process are protons (H^+) and lithium ions (Li^+) (Usha et al., 2016). Electrochromic bleaching and coloration activity in NiO_x thin films arise from the intercalation and extraction of 3 d electrons located in the valence band with no influence in the metal–oxygen bond. Then the charge transfer from Ni^{2+} to Ni^{3+} sites results in optical absorbance from the colored state (Dong et al., 2018).

The electrochromic reaction of NiO_x is represented by a two-step reaction process in Li^+ -ion electrolytes:



The first irreversible reaction (Eq. 2.3) is related to the activation process in the initial cycling of NiO_x . Then the second reaction (Eq. 2.4) shows the reversible coloring process when ions are intercalated/deintercalated and is associated to charge transfer between Ni^{2+} and Ni^{3+} states (Liu et al., 2018). Therefore, careful control the proportion of Ni^{2+} and Ni^{3+} ions plays a crucial role in improving the electrochromism of NiO_x (Qiu et al., 2018).

2.3 Transparent Conductive Oxides (TCOs)

Transparent conductive thin films (TCTFs) are extensively employed in technological devices such as computer displays, smartphones, TVs, tablets, optoelectronic devices, smart windows and so on. Tin-doped indium oxide (ITO) is one of the most extensively used TCTF in electronic device applications and belongs to a group of materials called transparent conductive oxides (TCOs) (Bright, 2018). A TCO basically alludes to an electrically conducting film and optically transparent across most of the visible spectrum. TCOs are normally coated onto flexible substrates or glass, usually in forms of heavily doped transparent metal oxides (Bright, 2018; Minami, 2013; Koseoglu et al., 2015). Besides $In_2O_3:Sn$ (ITO), these materials also include $In_2O_3:Zn$ (IZO), $ZnO:Ga$ (GZO), $ZnO:B$ (BZO), $ZnO:Al$ (AZO), $ZnO:F$ (FZO), $SnO_2:F$ (FTO) and numerous codoped alternatives. Over the last few years, the applications of TCO have spread even further from photovoltaic components, low-e glass and transparent electrodes to critical constituent materials in meta-structures, flexible display as well as in transformation optics (Wang et al., 2019).

2.4 Electrolyte Materials

Electrolytes play a crucial role as the main ion conduction medium in several electrochemical devices, for example: fuel cells, supercapacitors, electrochromics devices, dye-sensitized solar cells, lithium batteries, etc (Wu et al., 2018). The ionic conductor layer is an essential part of an ECD, it separates both electrodes to avoid direct electrical contact between them, allowing mutual ionic exchange since it has to ensure high ionic transport between the working and the counter electrodes to balance the charges that come up from the redox processes (Alesanco et al., 2018; Thakur et al., 2012). An ideal electrolyte for applications in electrochromic devices should display high ionic conductivity, ideal zero electronic conductivity, chemical and electrochemical stability, thermal stability and high optical transparency in the bleached state. Electrolytes can be in either solid form, gel or liquid. Electrolytes are generally composed of at least one or more salts and liquid solvents which dissociate and supply mobile ions. These mixing salts are usually composed of lithium salts (e.g., lithium trifluoromethanesulfonate (LiCF_3SO_3), lithium hexafluorophosphate (LiPF_6), lithium perchlorate (LiClO_4)) dissolved in a polar solvent (e.g., water, acetonitrile, ethylene carbonate, propylene carbonate) (Alesanco et al., 2018; Mortimer et al., 2015; Thakur et al., 2012).

Electrolytes are generally categorized into liquid electrolytes, polymer electrolytes, solid inorganic electrolytes and ceramic electrolytes. Between them, polymer electrolytes have been attracting more attention in the last years because of their promising applicability in the arising energy storage devices. Among them are fuel cells, batteries, electrochromic devices and supercapacitors. The ion conduction in the polymer electrolyte is heavily effected by the electrolyte salt and salt/host polymer ratio. Some of the principal disadvantages encountered in liquid electrolytes against polymer electrolytes include leakage, corrosion and packing problem (Dubal et al., 2018; Mortimer et al., 2015; Senthilkumar et al., 2012).

The polymer electrolytes (PEs) should have the following physical, chemical, and electrochemical properties (Mortimer et al., 2015; Thakur et al., 2012; Winie et al., 2020):

- High ionic conductivity and electronically insulating ($\sigma_e < 10^{12} S cm^{-1}$) to facilitate ion transport and to minimize self-discharge. High ionic conductivity ease the ionic movement and can improve switching time of ECDs.
- Robustness against mechanical, electrical and thermal abuses to run over a wide interval of temperatures as heat may be released during the operating of the EDC and ensure that it does not effect in the degradation of the device itself.
- Wide operating potential range to guarantee the durability of the device upon cycling. A wide operating windows of working potentials applied to cycle the ECD have to be taken into account to ensure an operating process without any side reaction
- High cation coordination ability which allows coordination bonding interactions to occur with the metal cations.
- Chemical and electrochemical stability against undesired reactions with both electrodes and within the voltage range used for operation of the ECD.
- High optical transparency in the bleached state and good adherence to the adjacent electrochromic layers.
- Easy preparation, non-hygroscopic, low cost and environmental friendliness for the successful implementation and commercialization of ECDs.

PEs can be classified into three groups according to their physical state and composition: solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs) and composite polymer electrolytes (CPEs). SPEs are composed by salts dissociated in a polar polymer matrix that form an ionic conducting phase, electrolytes are characterized for being solvent-free. To obtain a GPE generally a large amount of solvents and/or liquid plasticizer are incorporated into a polymer matrix that is able of forming a stable gel with the polymer host structure. CPEs basically are formed by incorporating an ionic liquid or inorganic material to the GPE which can improve the mechanical and electrochemical characteristics of the polymer matrix, as well as improve the ion conductivity (Winie et al., 2020, Thakur et al., 2012).

2.5 Electrochromic Device

A typical electrochromic device (ECD) consists of 5 superimposed films: an ion conductive layer (electrolyte) between the principal EC layer and the secondary EC layer or ion-storage layer that are coated one by one on transparent conductive oxides (ITO, FTO, ZTO, etc) substrates (Liu et al., 2016). An ECD has a structure and behavior similar to a battery (Kraft, 2018); basically it means, if for example, a Li^+ ion electrolyte is employed, the ECD becomes in a Li^+ ion battery sandwiched by transparent electrodes that switch its coloration state to transparent or colored, displaying when the battery is discharged or charged respectively (Thakur et al., 2012). Basically for the fabrication of electrochromic devices, cathodically and anodically coloring materials which color under intercalation/deintercalation of small ions, respectively, are widely investigated (Liu et al., 2016).

In ECDs the primary EC layer has the highest coloration efficiency which is connected to the working electrode. The secondary EC layer serves as an ion storage layer and generally has lower coloration efficiency or without showing electrochromic behavior which is attached to the counter electrode. The primary and the secondary EC layers are separated by an ionic conducting medium or electrolyte which has to display ideally a zero electronic conductivity to avoid short circuits and possess a high memory effect (Thakur et al., 2012). There are different types of electrolytes that can be used in ECDs, such as polymer electrolytes, inorganic ion conducting thin films or liquid electrolytes. The M^+ ions have to be small and with fast mobility to be freely exchanged through an electric field. Protons (H^+), sodium (Na^+), potassium (K^+), lithium (Li^+) and recently aluminum (Al^{3+}) ions are found between the options of ions employed in the electrolyte for ECD (Kraft, 2018).

The conditions for a high performance electrochromic device are (Thakur et al., 2012; Kraft, 2018; Mortimer et al., 2015)

- Coloration Efficiency: The coloration efficiency (η) is employed to measure the coloration efficiency exhibited by the EC layers and it describes the ratio of change

in optical density ($\Delta(OD)$) at a specified wavelength (λ) to the inserted or extracted charge (Q) per unit electrode area [Ccm^2], expressed by the following equation:

- **Coloration Efficiency:** The coloration efficiency (η) describes the ratio of change in optical density ($\Delta(OD)$) at a specific wavelength (λ) or integrated over a wavelength range, to the inserted or extracted amount of charge (Q) per unit electrode area [Ccm^2], expressed by the following equation:

$$\eta = \frac{\Delta(OD)}{\Delta Q} \quad (2.5)$$

The optical density (OD) can be measured from the transmittance of light in the colored and bleached state T_c and T_b respectively at the specific wavelength:

$$\Delta(OD) = \log \left(\frac{T_b}{T_c} \right) \quad (2.6)$$

The ideal EC device or material has to display a large optical modulation with a small amount of charge, giving as a result higher CE and cyclic stability.

- **Contrast ratio:** Optical contrast ratio (CR) is employed to quantitatively estimate the intensity of color change in an electrochromic device. CR can make reference either to a specified wavelength or to the complete white light. For a transmissive ECD, CR is described by the equation

$$CR = \frac{T_b}{T_c} \quad (2.7)$$

where T_b represents the intensity of light transmitted in the bleached state and T_c represents the intensity of light transmitted in the colored state, being the air as reference.

In the case of reflective ECDs, CR is given by the equation:

$$CR = \frac{R_b}{R_c} \quad (2.8)$$

The above parameters are useful to characterize the contrast ratio at a single wavelength, as for example, at the specific wavelength of maximum human visual sensitivity (555 nm)

- **Switching Time:** is the required time to switch between different electrochromic states considering a specific wavelength, at 550 nm or at photopic transmittance. For practical applications high response time is of great importance. The speed of response time strongly depends on magnitude of the applied potential, ionic conduction of the electrolyte, ionic diffusion in the films, morphology and thickness of the films.
- **Write-Erase Efficiency:** It refers to the percentage of the initially formed coloration state that can be subsequently and reversibly bleached.
- **Cycling life:** high cycling life in ECDs is one of the most important characteristics. When a ECD is repeatedly cycled between the differently colored oxidation states the cycling life decreases as consequence of chemical side reactions or physical modifications in solid phases that affect the electrode composition. A good cyclic durability means switch between the colored and bleached (and intermediate) states several times with no significant modification in switching speed, switching potential and no cosmetic or superficial defects such as non-switching areas, uneven bleaching or coloring, delaminations, etc. In glazing for building applications a minimum of 10^5 working cycles is generally specified

In this thesis, the ECD is composed of WO_3 as cathodic electrode and primary electrochromic layer, NiO_x as anodic electrode and secondary electrochromic layer, and LiClO_4 -PC as electrolyte and ITO as transparent conductive oxide electrodes.

For the configuration in this ECD, optical modulation arises when Li^+ are transported between the cathodic coloring WO_3 and anodic coloring NiO_x followed by charge-balancing injection/ejection of electrons and ions under an applied bias to the ITO

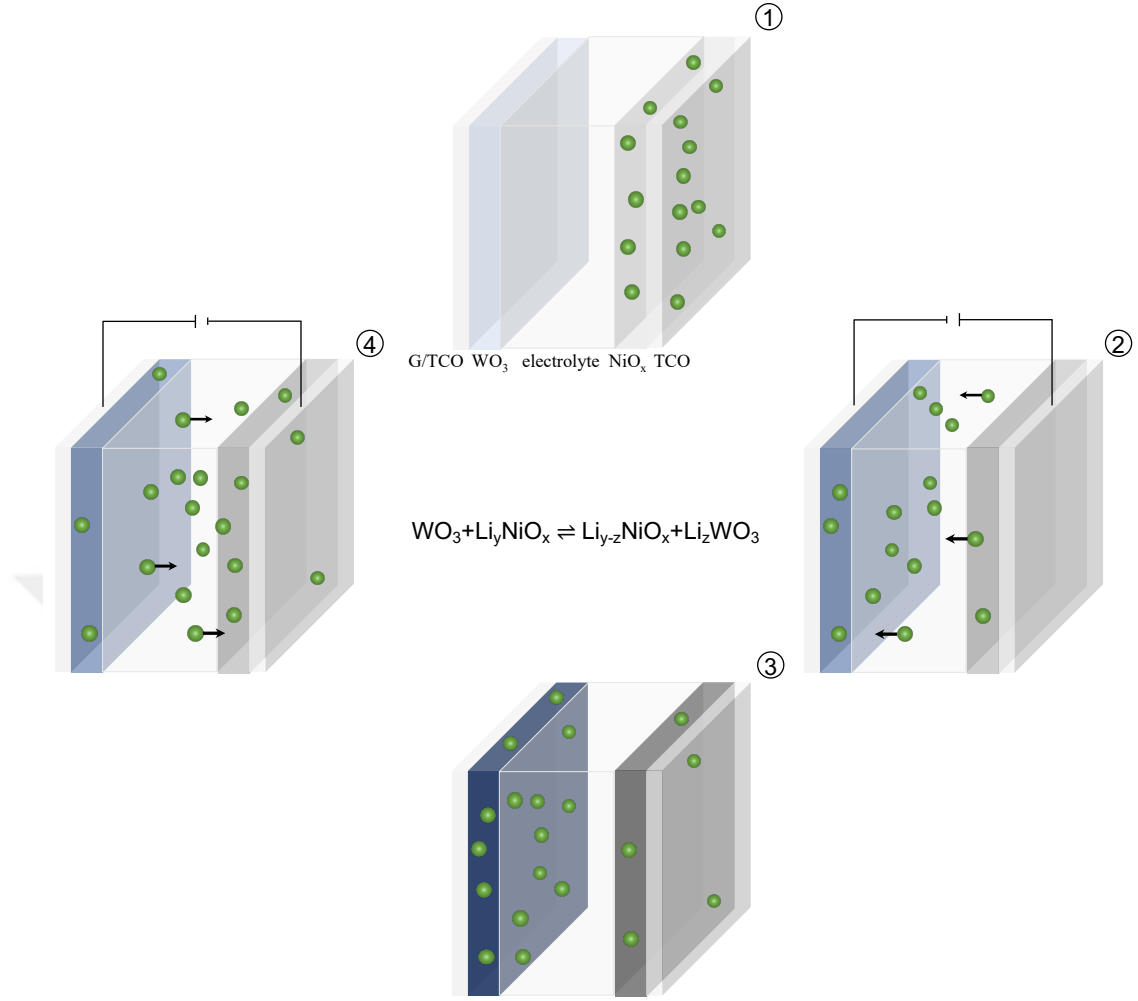


Figure 2.5 During discharge driven by the built-in cell voltage, Li^+ are released from the already activated Li_yNiO_x anode, migrating through the electrolyte and inserted into the WO_3 cathode. The injection of Li^+ ions causes the reduction of the WO_3 primary electrochromic layer and changes the cathode color from colorless to a colored dark blue Li_zWO_3 layer, at the same time the oxidation of the Li_yNiO_x secondary EC layer occurs, changing the anode color from colorless to a gray colored $\text{Li}_{y-z}\text{NiO}_x$ layer. In the bleaching process, a reverse bias is applied to extract Li^+ from the lithiated Li_zWO_3 cathode, yielding to the initial WO_3 and Li_yNiO_x transparent layers. Figure adapted from (Cheng et al., 2018)

transparent electrodes. The optical transmission of the electrochromic device can be repeatedly reversed by exchange of charges and electrons. Also the electrochromic properties should remain constant without any defect arising inside the device. To achieve this, the intercalation and extraction of Li^+ in the electrochromic layers is influenced principally by surface, structure, porosity and composition (Dong et al., 2018).

2.6 Sputtering Deposition Method

Due to the potential applications of the WO_3 and NiO_x metal oxides in EC applications, they likely imply thin films and a extensive number of deposition methods have been developed to synthesize thin films. According to the deposition nature, thin film deposition methods can be generally branched into chemical vapor deposition (CVD) and physical vapor deposition (PVD). Among the CVD techniques are sol–gel method, thermal oxidation, spray pyrolysis and various post-deposition processes. Among the PVD available to produce EC films are pulsed laser deposition, reactive evaporation, reactive sputtering in argon and oxygen environment from a metal target. The PVD methods of vacuum sputtering and evaporation are likely the most controllable, giving the best quality thin films (Ramanathan, 2014; Moorthy, 2015).

Physical sputtering is one technique of PVD which basically consists in the physical ejection of atoms, clusters of molecules or atoms from a solid target material by momentum transfer when is bombarded by inert incident gas ions (Mattox, 2018). The ionization of the inert gas (generally argon) takes place under vacuum conditions between the substrate (anode) and sputtering target (cathode) which is maintained at high potential. A variety of sputtering systems have been developed with the aim to synthesize thin films including radio frequency (RF) sputtering, direct current (DC) sputtering, DC magnetron sputtering, and ion beam deposition (Mattox, 2018; Wasa, 2012).

In DC magnetron sputtering, basically the secondary electrons ejected from the target are more efficiently used resulting in the principal source to ionize the sputter gas. For this propose DC magnetron sputtering consists of integrated permanent magnets or electromagnets which create superposed magnetic field lines parallel to the target plane which results in an $\vec{E} \times \vec{B}$ drift path or "racetrack", where $\vec{E}$ express the electric field during the discharging process and $\vec{B}$ the superposed transversal magnetic field (Wasa, 2012; Seshan, 2012). After achieving the desired working pressure of the sputter gas, a negative DC bias with high voltage is supplied to the sputtering target (cathode) (Moorthy, 2015). Since the high electric field, E arising from the cathode is perpendicular to the applied magnetic field, B then a perpendicular drift velocity $\frac{\vec{E}}{B}$

acts on the secondary electrons in the glow discharge, traveling confined in a cycloid motion close to the target surface, which results in an increase of the ionization process of the sputter-gas atoms which effects in an increment of the plasma flux density close to the target surface (Seshan, 2012; Gatzen et al., 2015). This process increases the density of current at the target, efficiently increasing the sputtering yield during the thin film deposition (Moorthy, 2015).

Normally deposition processes are carried out in an argon ambient. After achieving the desired working pressure of the sputter gas, a negative DC bias with high voltage is supplied to the cathode. Then with the aim to deposit a compound between the sputtered material atoms (such as metals) and the reactive gas molecules, a reactive gas such as O_2 is sent to the vacuum chamber to carry out the reactive sputtering process. The incorporation of a reactive gas in the chamber changes the behavior of the sputter deposition process significantly. The reactive gas will strongly affect both the deposition rate and the composition of the thin films. Another advantage of this deposition technique is that by adjusting the reactive gas flow, the stoichiometry of the thin films can be controlled during the deposition process. (Gatzen et al., 2015; Depla & Mahieu, 2008).

In the course of this work reactive DC magnetron sputtering technique is employed for the deposition of the metal-oxide thin films series.

2.7 Physical Characterization

2.7.1 Scanning Electron Microscopy (SEM)

SEM has become in a key technology for the morphological characterization of materials over a extensive range of industries since it can be employed for analyzing the microscopic characteristics of thin films, for example: grain boundaries, porosity and surface morphology (Moorthy, 2015). The basic principle in SEM, consists of emitted electron beams from an electron gun by thermionic heating of the tungsten filament or by high vacuum field emission cathode, then are focused by the condenser

and objective lenses to a point, subsequently they are scanned by coils sequentially across the surface of the specimen or sample. The typical energy of the accelerated electrons are $1 - 30\text{keV}$ (Inkson, 2016; Moorthy, 2015). When the emitted electrons interact with the specimen, they generate secondary electrons, backscattered electrons, and characteristic X-rays. Then these signals emitted from the sample at each location are collected by the detectors. The signal detector is synchronized with the known location of the electron beam in the specimen, and the intensity of the signal is used to modulate the corresponding image pixel. Finally, the serially collected signals are combined to form an image in pixel/dimensions distribution depending on the chosen scan pattern (Inkson, 2016; Shuster et al., 2019).

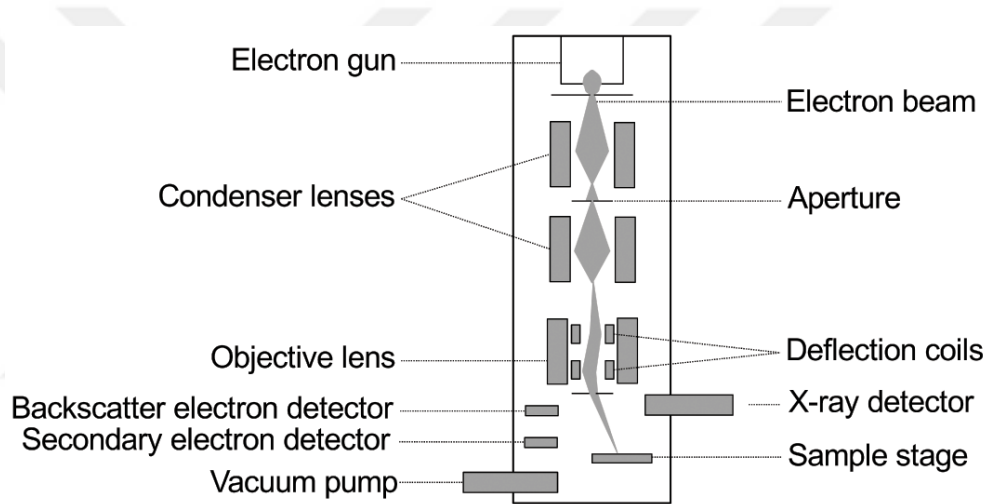


Figure 2.6 A schematic diagram of an SEM illustrating the pathway of an electron beam that is focused by condenser lenses and moved in an x or y-direction by deflection coils (Shuster et al., 2019)

2.7.2 X-Ray Diffraction (XRD)

XRD is an extensively used method to describe the crystalline structure of materials. The wavelength of the X-rays belong to the electromagnetic spectrum in the range of $0.1-100\text{ \AA}$ (Moorthy, 2015). XRD non-destructive technique (between a few of them) that can directly measure the deformation in the crystal lattice of epitaxial films (Seshan, 2012). When scattered waves interfere constructively in XRD, a peak is shown. The connection between the wavelength λ of the monochromatic incident X-ray beam,

the set of atomic planes of the crystalline lattice with distance d (Figure 2.7) and the angle of diffraction θ is derived by the Bragg equation:

$$n\lambda = 2d \sin \theta \quad (2.9)$$

where $n = 1, 2, \dots$ describes the diffraction order (Moorthy, 2015; Borisenko & Ossicini, 2012). The interplanar distance of the sets can be deduced easily from this equation. By analyzing the intensity of X-ray scattering from various crystal planes is possible to reconstruct the complete structure of a solid (Borisenko & Ossicini, 2012).

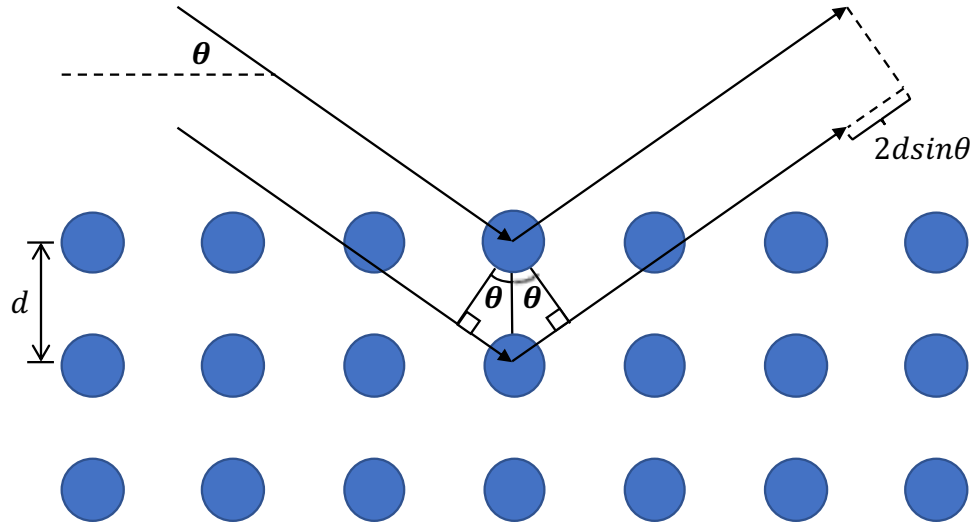


Figure 2.7 Constructive interference of x-ray diffraction

2.7.3 X-Ray Photoelectron Spectroscopy (XPS)

XPS is characterized for being a quantitative and nondestructive technique that allows to determine the quantification of elements, chemical bonds, oxidation states, atomic composition of the sample and determination of contaminants (Yahia & Mireles, 2017). The photoelectric effect is the basic principle in this characterization method.

In XPS the sample to be analyzed is exposed to irradiation coming from a high energy source of X-ray photons in a range from 100 eV to 10 eV (Borisenko & Ossicini, 2012). To allow the surface analysis of the sample, the X-rays penetrate only 1–10 nm

under the surface (depending on the inclination angle of sample) (Yahia & Mireles, 2017). The X-ray beam of known wavelength incident on the sample surface induces core electrons (K -shell) ejection from the specimen, following absorption of incident photons from an X-ray source causing an electrons with binding energies (E_B) to be moved away from an atomic orbital or band to reach the vacuum level (as is depicted in Figure 2.8). The ejected electrons (e^-) have a kinetic energy (E_K) that is associated to the energy of the incident ray $h\nu$, binding energy of the electron (E_B) and the work function (ϕ_{sp}) of the spectrophotometer (Yahia & Mireles, 2017; Aziz & Ismail, 2017). This relation can be represented by the expression

$$E_K = h\nu - E_B - \phi_{sp} \quad (2.10)$$

By using an electron energy analyzer, a record of the photoelectron spectrum can be obtained from the distribution of the kinetic energy of the emitted photoelectrons (that is, the number of photoelectrons emitted as a function of E_K). The number of electrons identified in the XPS detector is proportional to the concentration of the element, so that once the background is removed, the peak areas can be used with empirically derived sensitivity factors to quantify particular elemental species (Engelhard et al., 2017). In this way it is possible to find which elements are close to the surface of the material, the binding energy of the electron and their chemical states (Aziz & Ismail, 2017).

2.8 Electrochemical Characterization

Electrochemistry is a strong tool used to study electrochemical reactions concerning electron or ion transfers under various electrochemical conditions. This can be employed for an extensive range of applications. For example: capacitors, batteries, sensor studies, electrochromic devices, etc (Choudhary et al., 2017). The vessel used for carrying out the electrochemical characterization is called electrochemical cell, schematically represented in Figure 2.9. A basic configuration and essential elements

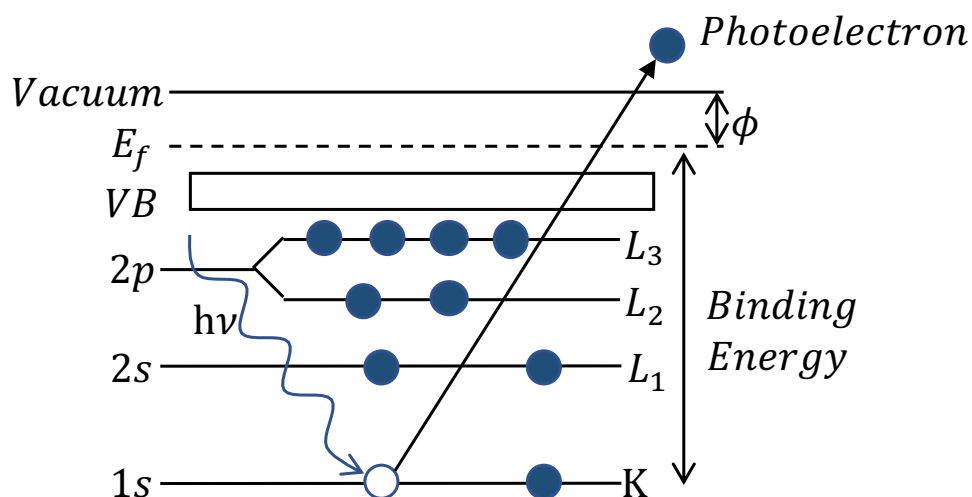


Figure 2.8 Basic principle of photoemission in X-ray photoelectron spectroscopy

of a three-electrode electrochemical cell includes (Elgrishi et al., 2017; Napporn et al., 2018):

- Working Electrode (WE): It performs the electrochemical process of interest. Throughout this thesis the electrochromic films serve as WE whose oxidation and reduction of this metal-oxide thin film is the process of interest.
- Reference Electrode (RE): Is employed in an electrochemical cell as a reference point against the potential of other electrodes. A RE is characterized for having an equilibrium potential well defined and stable.
- Counter Electrode (CE): It is an auxiliary electrode whose purpose consists of completing the electrical circuit and allow charge to flow. The current is recorded during the flow process of electrons between CE and WE. Then when a reduction reaction of interest occurs at the WE, at the CE an oxidation reaction occurs. For this reason an inert CE such as Platinum, Gold or Carbon has to be chosen.
- Solvent: It generally has a high dielectric constant to allow the electrolyte to be dissolved and allow the flow of current. It is stable during the reduction and oxidation process in the range of the potential applied in the experiment.

- **Supporting Electrolyte:** It supplies the pathway for the flow of ions or electrons within the electrochemical cell. It should be chemically and electrochemically inert under the conditions of the experiment and highly soluble in the specified solvent.

In the conventional three-electrode system, the potential is measured between the working and reference electrodes meanwhile the current flow is measured through the counter and the working electrodes. The measurement of potential, current or charge in electrochemical characterization is employed to determine the concentration of an analyte or to determine the chemical reactivity of an analyte. The basic electrochemical signals are potential, current and charge which act as analytical signals. Therefore, for all the electrochemical characterization techniques, these signals conform the central experimental design (Choudhary et al., 2017). Among several electrochemical characterization techniques, cyclic voltammetry (CV) and chrono-amperometry (CA) are used through this thesis.

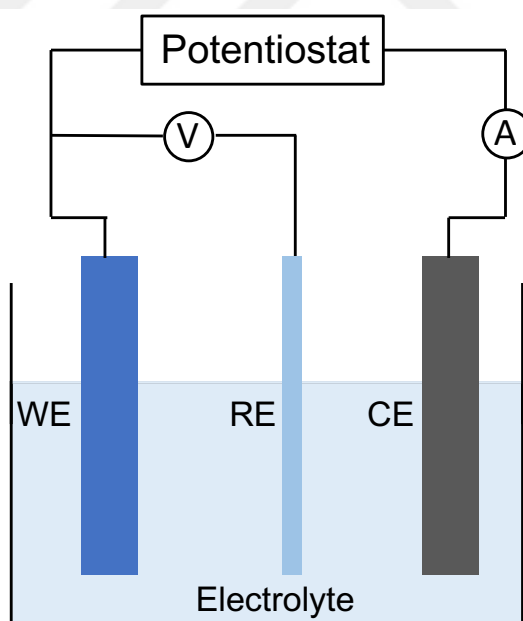


Figure 2.9 Schematic representation of a conventional three-electrode electrochemical cell

2.8.1 Cyclic Voltammetry (CV)

CV is a popular and powerful electrochemical method commonly used to study the oxidation and reduction reactions of electrochemical systems (Elgrishi et al., 2017). The fundamental concept of CV relies on the application of a linear variation of the potential $V(t)$ to the working electrode at a fixed scan rate between an starting value V_1 and a final value V_2 , then when the fixed potential reaches V_2 the scan is reversed and the potential is swept back to V_1 , recording the electrochemical response as an electric current $I(t)$, and repeating it cyclically, as long as necessary (Napporn et al., 2018; Choudhary et al., 2017). In CV the scan rate controls how fast the applied potential is scanned in the experiment, commonly represented in Vs^{-1} . The plot of the current response versus voltage is the specific signature of a material cycled in a given supporting electrolyte, and is called "voltammogram" (Figure 2.9). Faster scan rates of the CV in the experiment result in higher currents, since there is a diminution in the dimensions of the diffusion layer. This technique has been widely employed for studying the reversible oxidation/reduction behavior of electrochromic materials since it provides qualitative and fundamental information about the reversibility of the oxidation/reduction reaction processes, as well as about the speed of the involved systems (Napporn et al., 2018).

2.8.2 Chrono Amperometry (CA)

The basic principle of CA consists of applying a specific potential instead of a potential scan (Pinto et al., 2018). The working electrode potential is changed drastically and immediately from a potential V_1 to a potential V_2 , at the same time that the response of the electrical-current is continuously tracked as a function of time (Westbroek, 2005). The CA finds its applications in the field of electrolysis, metal deposition and the investigation of electrochemical systems and their stability over time. The potential to be applied for a CA process has to be the result of preceding voltammetric studies (Napporn et al., 2018). In the study of EC materials and ECD, CA is employed to study the response time, cycling durability and reversibility between different redox potentials.

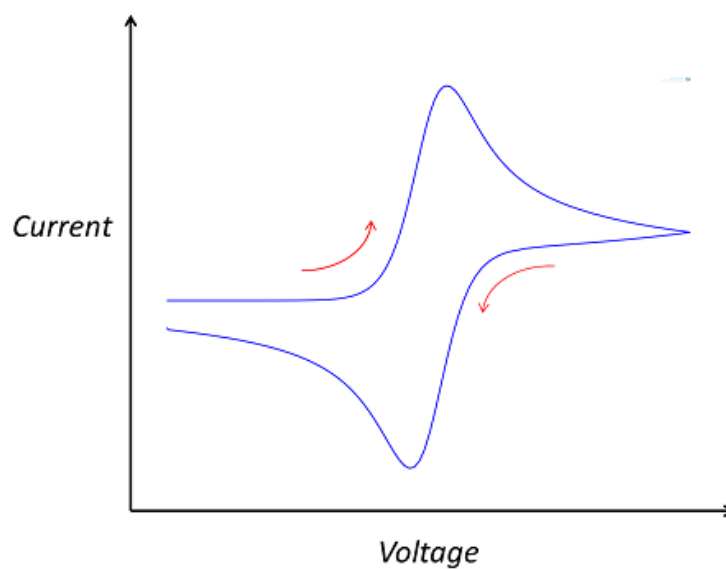


Figure 2.10 Schematic representation of a typical voltammogram in CV (Forrister, 2018)

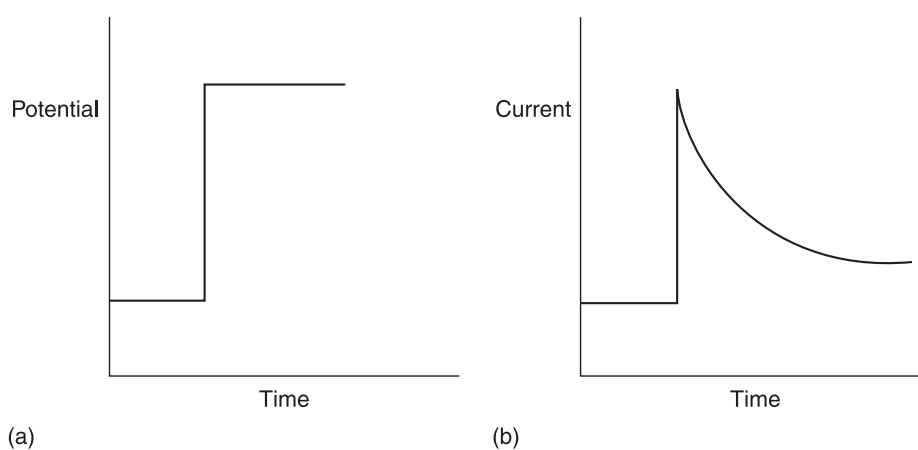


Figure 2.11 (a) Excitation waveform and (b) response waveform in chrono amperometry

CHAPTER THREE

EXPERIMENTAL PROCEDURES

3.1 Thin Film Deposition

In this work the deposition process for all metal-oxide thin film layers was performed by reactive DC magnetron sputtering since in comparison with chemical deposition methods, DC magnetron sputtering technique provides good reproducibility and a one-step deposition of films with good adhesion and uniform thickness.

Besides the chosen deposition technique the deposition of the EC metal oxide thin films, an off-axis configuration for the deposition process was employed. This design unlike on-axis sputtering deposition, allows to settle the samples at outside of the discharge plasma and protects the substrate and thin films during the growing process from high-energy particle bombardment resulting from the sputtering deposition process. This technique minimize the damage from that negative ions coming from the bombardment, resulting in low defect films since it is simple to control the kinetic energy of the sputtered particles/atoms arriving to the surface of the film in process of deposition (Zhu et al., 2000).

Off-axis sputtering technique also allows a slower deposition rate than on-axis sputtering technique and also may help to use slower working pressures to get porous thin films. The thickness distribution along the substrate holder will be higher just above the center of the target and it will decrease radially uniform along the substrate holder. For this reason besides the off-axis configuration, under a suitable design the substrates were placed on the holder with an oblique angle geometrical configuration. Another advantage is that in our sputter deposition system up to 10 samples can be deposited at the same time.

The sample setup was made in a 15x15 cm area sample holder. Prior to the deposition process, ITO coated microscope slides with dimensions 76x26 mm were cut in half with a diamond cutter. The 38x26 mm glasses were fit in the holder by using 20 mm binder clips to hold the samples. In order to reserve free ITO electrodes in

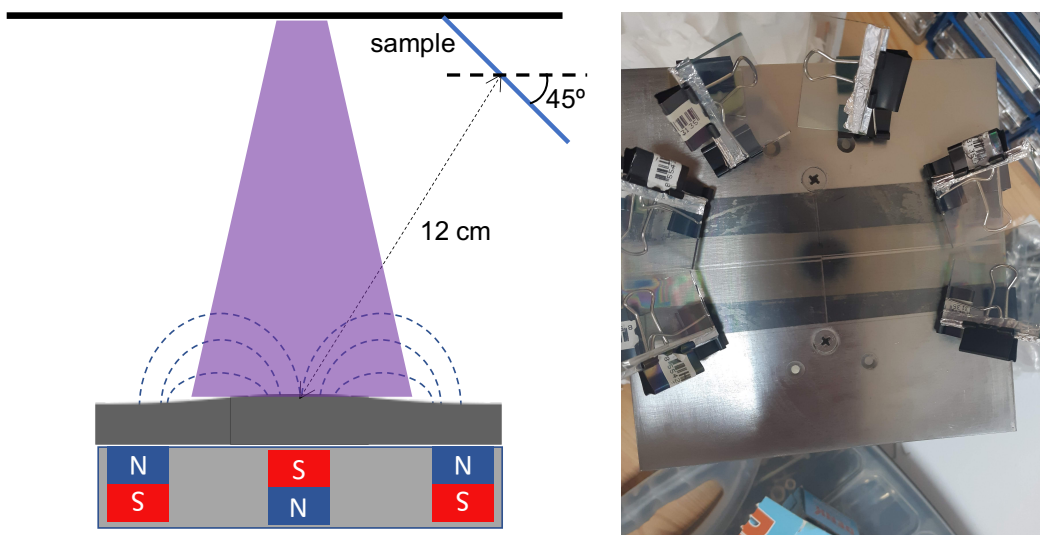


Figure 3.1 Left side: Schematic view of the sample setup for the deposition of the electrochromic and thin films. Right side: A picture of the substrate holder arrangement previously to place it inside the chamber (Personal archive, 2019)

the samples for electrochemical measurements, prior the sputtering process, aluminum foil was attached to the edge of these substrates before the deposition. The distance target-substrate in this off-axis sputtering arrangement is 12 cm with an angle $\alpha = 45^\circ$ respect the horizontal as is shown in Figure 3.1.

The WO_3 and NiO_x thin films series were deposited separately on 180 nm thick ITO coated glasses whose resistivity is $R=16 \, \Omega/\square$ and dimensions are 38x26 mm. The thin film metal oxides were coated employing reactive DC magnetron sputtering technique where a 50.8 mm diameter pure tungsten (99.9% purity) and nickel (99.9% purity) were used as metallic cathode in the sputter gun. First the ITO coated glasses were set up inside the chamber as was explained before. Then the sputtering chamber was evacuated to high vacuum conditions with a base pressure of 7.5×10^{-6} Torr. Before the deposition the W and Ni-targets were presputtered for 5 minutes using only Ar with the shutter above the sputter gun closed. Subsequently, under a reactive process of argon and oxygen atmosphere, a stable working pressure during the deposition process and a constant DC power. The deposition parameters of the thin film series are summarized in Table 3.1. The flow rate of Ar and reactive flow rate of O_2 were adjusted independently by a mass flow controller and the thicknesses of the thin film series were

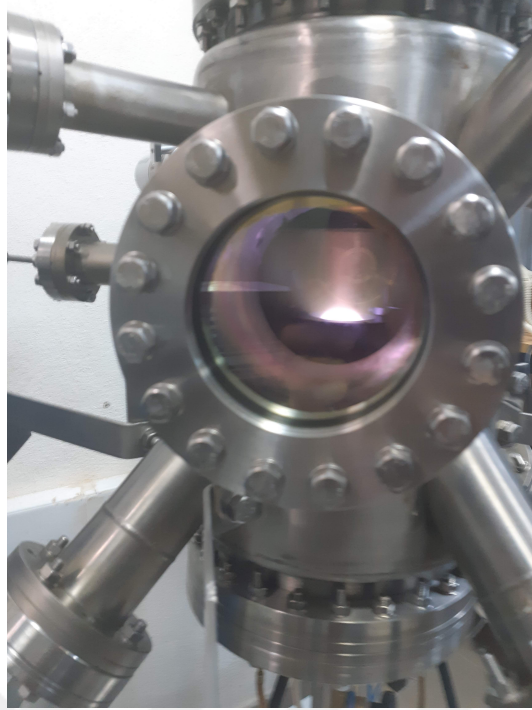


Figure 3.2 DC magnetron sputtering system at the Physics Department in Izmir Institute of Technology (Personal archive, 2020)

controlled by adjusting the deposition time. All thin films in this work were deposited employing this design.

Table 3.1 Detailed experimental parameters of the WO_3 and NiO_x thin films

Film	Target	Ar:O ₂ (sccm)	Working Pressure (Torr)	Power (W)	Sputtering Time (min)
NiO _x	Ni	100:2	5.6×10^{-3}	40	40, 50, 60, 70
WO ₃	W	90:30	7.2×10^{-3}	50	40, 50, 60, 70

3.2 Material Characterization

3.2.1 Thickness Measurement by Profilometry

Thicknesses of the thin film series were controlled by deposition time and were determined by surface profilometry using a Veeco DEKTAK 150 Profilometer instrument. This surface profilometer measures the thickness of the thin films by running a diamond tipped stylus along the surface over the step between un-coated and coated sample areas while measuring its vertical displacement. Before the deposition process, a sample was dropped with photoresist, then after the deposition process photoresist was removed by using acetone in ultrasonic bath and then cleaned with DI water.

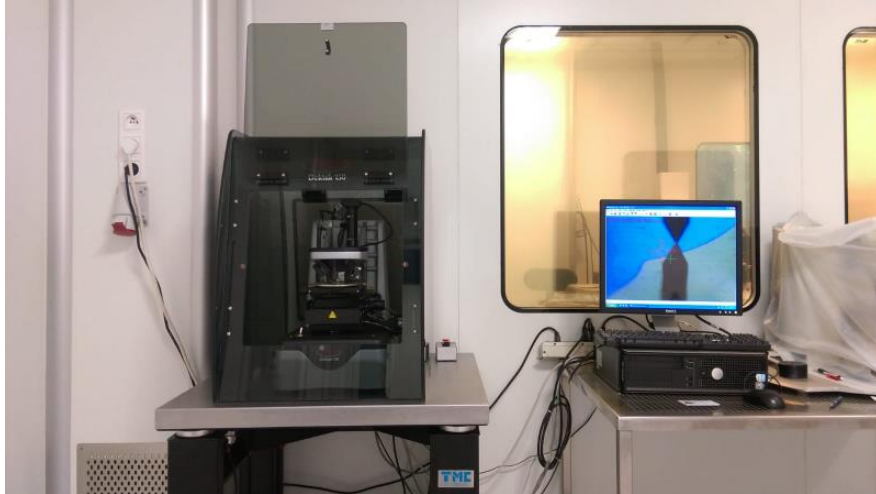


Figure 3.3 Profilometry measurements at the Physics Department in Izmir Institute of Technology (Personal archive, 2020)

3.2.2 Scanning Electron Microscopy

In order to understand the morphology and structure of our thin film series deposited by reactive DC magnetron sputtering and employing an off-axis deposition technique, scanning electron microscopy (SEM) studies of all thin film samples without any post-deposition annealing or treatment were performed under high vacuum conditions with a FEI QUANTA 250 FEG device at 15 kV and different magnifications.

3.2.3 Structure Analysis by XRD

In order to analyze the crystalline structure of the electrochromic metal-oxide thin film series deposited by reactive DC magnetron sputtering at room temperature, x-ray diffraction analysis has been performed. Crystallographic information of the films was obtained by an X-ray diffractometer Philips X'Pert with CuK_α radiation ($\lambda=0.154 \text{ \AA}$). The x-ray diffraction was recorded between $10 < 2\Theta < 90$.

3.3 Electrochemical Analysis

Electrochemical characterization is a very useful tool to study electrochemical reactions involving electron or ion transfers under various electrochemical conditions. Cyclic voltammetry (CV), chrono amperometry (CA) and electrochemical impedance spectroscopy (EIS) are employed throughout this thesis.

CV and CA were recorded in order to evaluate the electrochemical performance during the insertion/extraction of Li^+ ions. Electrochemical characterization for glass/ITO/ WO_3 and glass/ITO/ NiO_x series were performed in a conventional three-electrode electrochemical cell, using a potentiostat/galvanostat Gamry 600 electrochemical workstation. The electrochemical cell consists of a working electrode (sample), a Ag/AgCl reference electrode and a Pt foil as counter electrode, as is illustrated in Figure 3.3.

Earlier works have demonstrated that LiClO_4 -PC electrolyte is suitable for WO_3 and NiO_x thin films. The electrodes were immersed into glass beaker containing the electrolyte solution of 1 M LiClO_4 in propylene carbonate (PC) which provides mobile Li^+ ions (chemicals purchased from Acros Organics). The effective geometrical area of the working electrode in the solution was $1.5 \times 2 \text{ cm}^2$. The CV tests were achieved at a scan rate of 100 mV/s over the potential range of -1.2 and 1.0 mV/s and -0.5 and 1.5 mV/s for the WO_3 and NiO_x thin film series respectively.

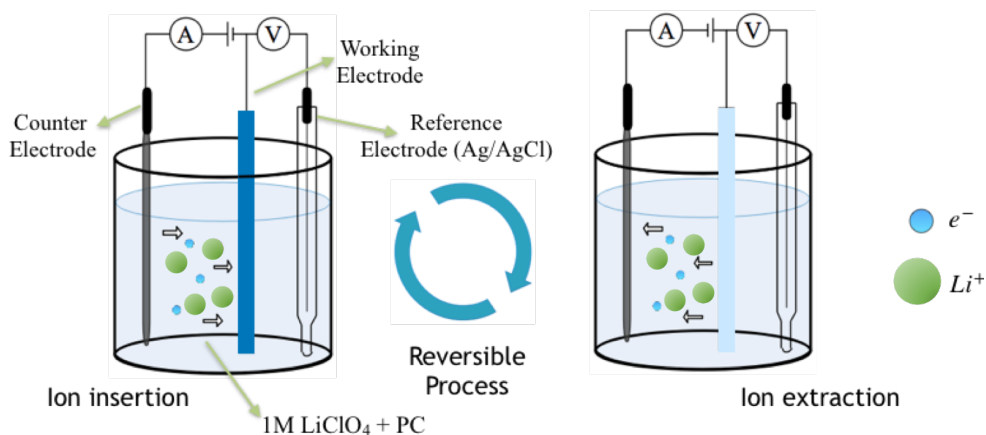


Figure 3.4 Schematic setup of a conventional three-electrode electrochemical cell used in this thesis

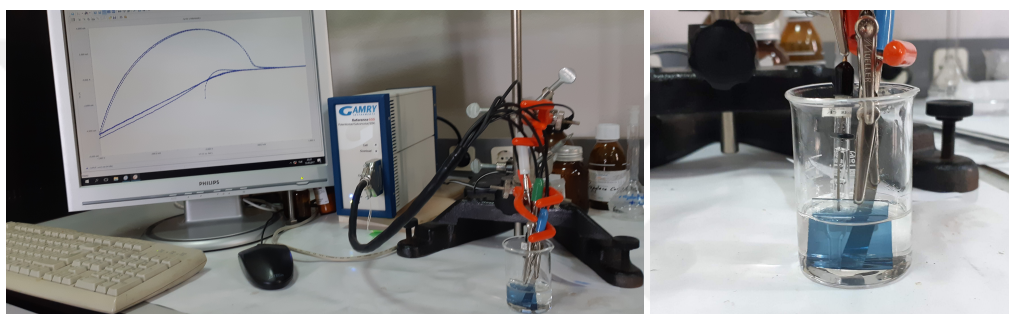


Figure 3.5 Left side: CV plot during experiment. Right side: 3-electrode configuration for electrochemical characterization (Personal archive, 2019)

3.4 Optical Transmission

In this study, *ex-situ* (out with the electrochemical cell) measurements of optical transmittance are achieved on cathodic WO_3 and anodic NiO_x thin films coated on ITO/glass. Before the optical transmission measurement, during the electrochemical process the CV was stopped when the current density was zero and the cycle was to be reversed at the fully colored or bleached state, then the sample was taken out of the electrolyte, washed and cleaned with de-ionized water and placed in the spectrophotometer. The transmittance was then recorded by a double beam UV-VIS-NIR Perkin Elmer Lambda 950 in the $200 < \lambda < 2600$ wavelength range with a scanning speed of 993.61 nm/min.

CHAPTER FOUR

RESULTS

4.1 Tungsten Oxide

4.1.1 Physical Properties

It is well known that as-deposited electrochromic a-WO₃ are transparent thin films are optically reversible under insertion/extraction of ions. In this work transparent as-deposited WO₃ thin film were obtained. Table 4.1 shows the thickness corresponding to the different deposition times, determined by surface profilometry.

Table 4.1 Thickness of WO₃ thin films with different deposition times on the glass/ITO substrates

Sample	Sputtering Time (min)	Thickness (nm)
WO ₃ -1	40	249.29
WO ₃ -2	50	331.89
WO ₃ -3	60	397.98
WO ₃ -4	70	476.77

4.1.1.1 SEM

To understand the structure, morphology and surface property of our deposited thin films SEM analysis was done. The top-view SEM image for the ~300 nm-thick magnetron sputtered WO₃ thin films deposited on ITO/glass without any post-deposition annealing or treatment is shown in Figure 4.1. This SEM images were obtained before electrochemical characterization

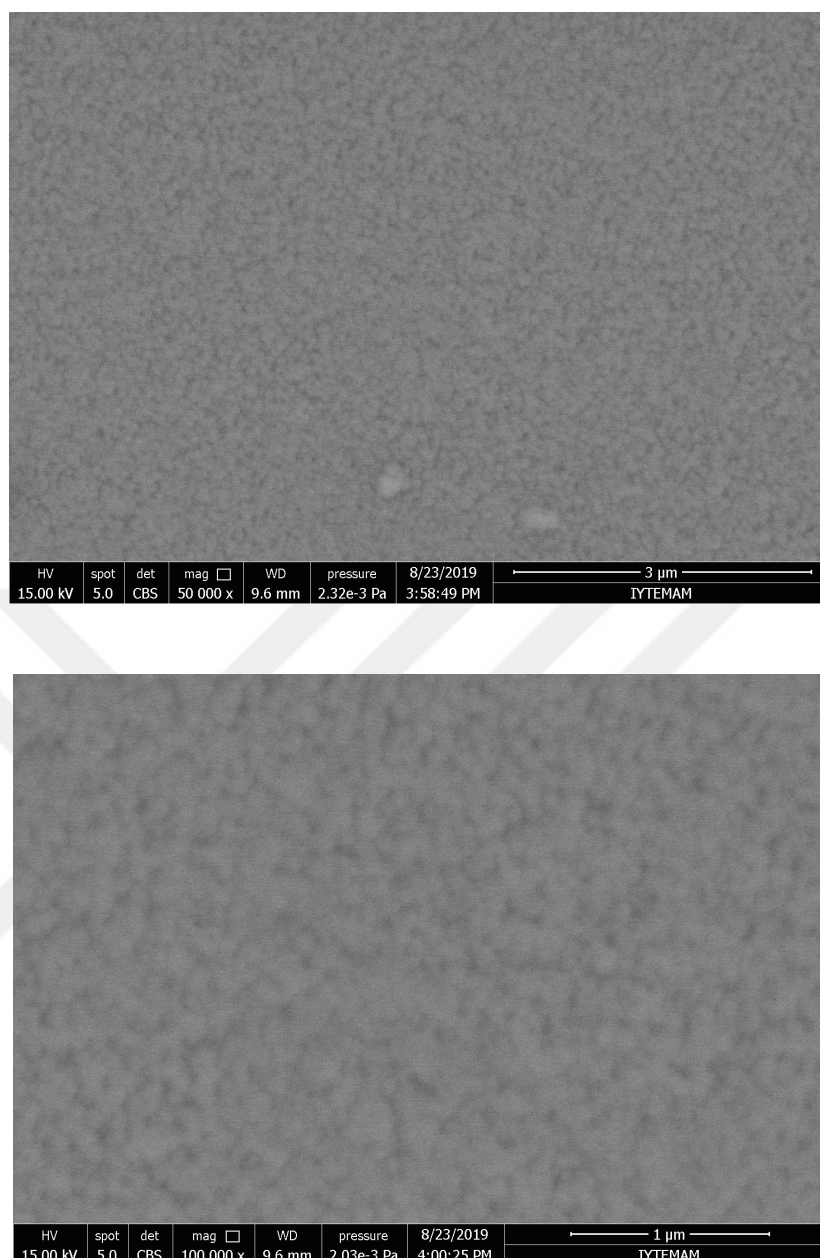


Figure 4.1 Top-view SEM images of the magnetron sputtered WO₃ thin films deposited on ITO/glass where an uniform morphology can be observed

4.1.1.2 XRD

The x-ray diffraction patterns for the ~300 nm-thick magnetron sputtered WO₃ thin films deposited on ITO/glass are shown in Figure 4.2. XRD showed no diffraction peaks, since there was no external thermal energy provided, amorphous WO₃ thin film series were deposited satisfactorily under the selected conditions. Is well known that

for EC applications, amorphous WO_3 thin films display higher coloration efficiency and faster response time than crystalline structured WO_3 thin films.

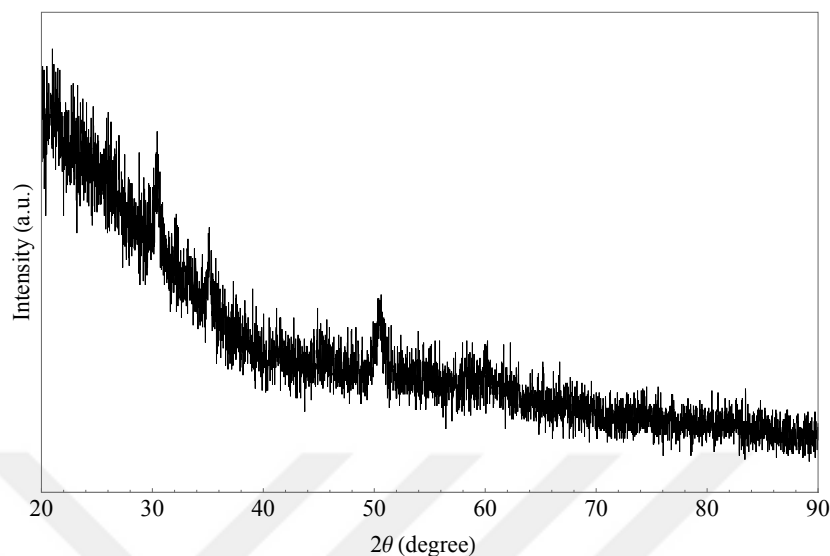


Figure 4.2 X-ray diffraction data of a magnetron sputtered WO_3 thin film, deposited onto ITO/glass displaying only an amorphous characteristic

4.1.2 Electrochemical Properties

The WO_3 was electrochemically cycled in 1M LiClO_4 -PC electrolyte in a potential range of -1.2 to 1.0V vs Ag/AgCl for electrochemical testing. Figure 4.3 shows the voltammogram at the scan rate of 100 mV/s. As is observed in the WO_3 thin films, the higher the film thicknesses, the more current flows through the thin film, and thus the higher anodic and cathodic peak current intensities. So charge capacity depends strongly on sample thickness and also greater amount of Li^+ ion insertion increase when potential range is increased (Figure 4.4).

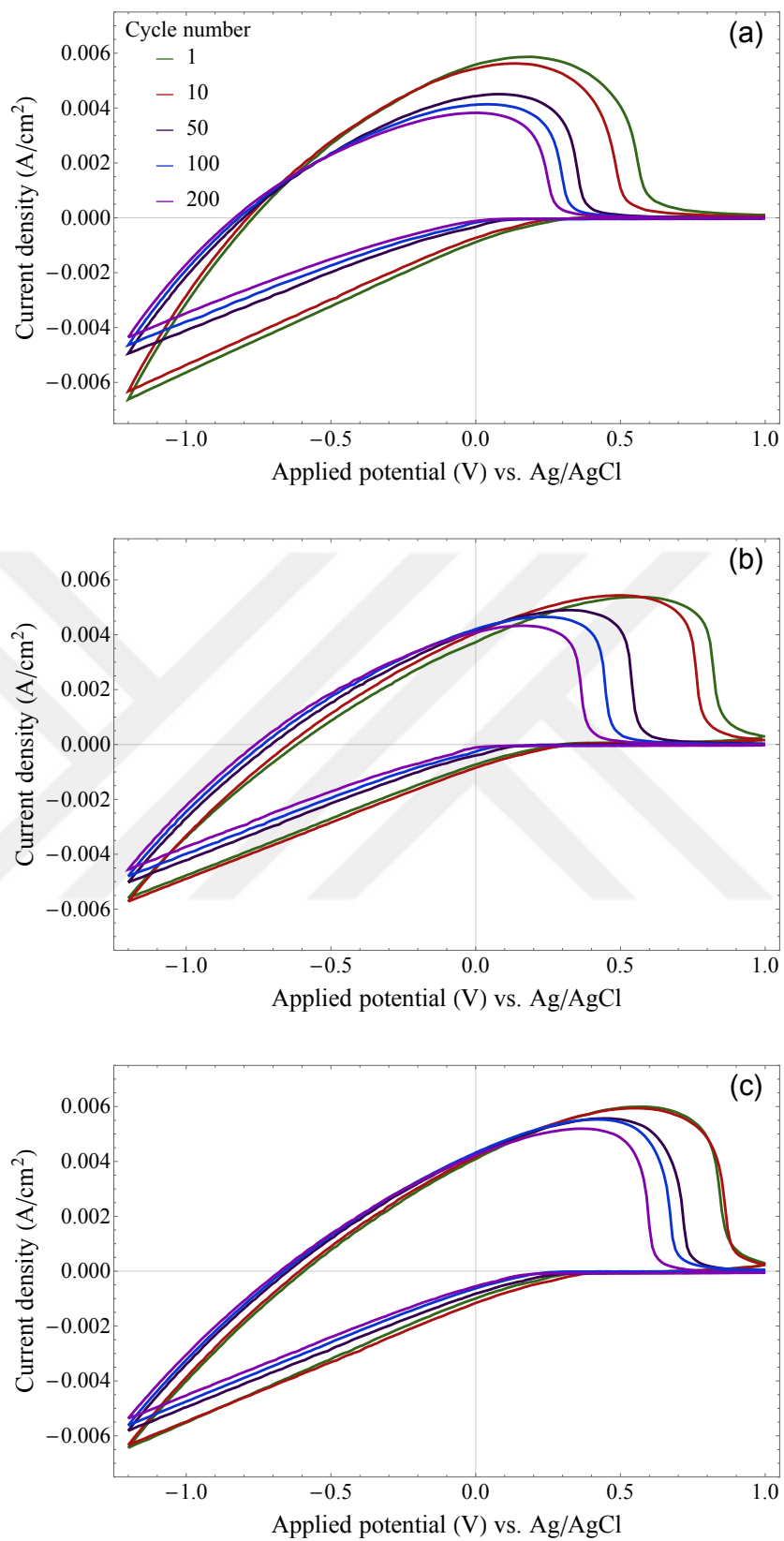


Figure 4.3 Evolution of the CVs at the cycle 1, 10, 50 100 and 200 with different thicknesses (a) WO₃-1, (b) WO₃-2, (c) WO₃-3 and (d) WO₃-4 immersed in 1 M LiClO₄-PC electrolyte

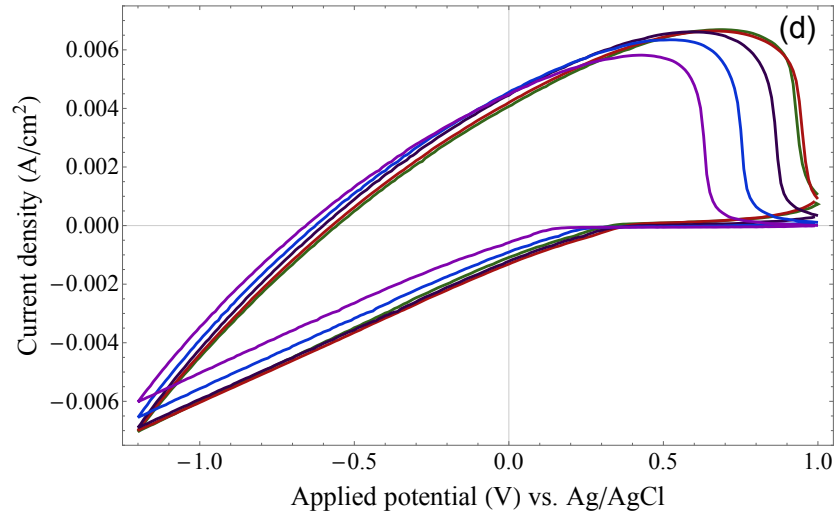


Figure 4.3 continues

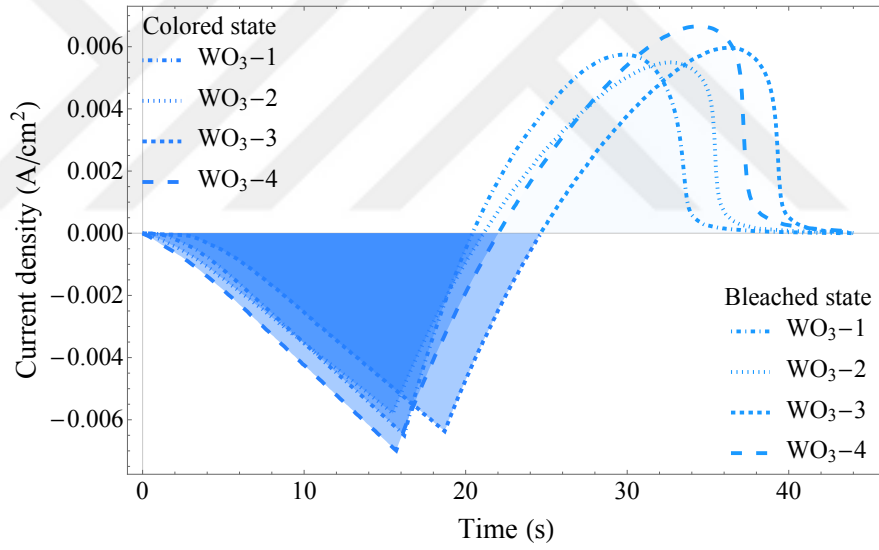


Figure 4.4 Evolution of the current density basing on the 20 time CV measurement at 100 mV/s with different thicknesses of WO₃ thin films

The diffusion coefficient D of Li^+ ions in the WO₃ thin films was obtained from the Randles-Servick Eq.

$$J_p = 0.4463nFAC\left(\frac{nFvD}{RT}\right)^{\frac{1}{2}} \quad (4.1)$$

where J_p is the peak current, F Faraday's constant (96485 C/mol), n number of electrons, A electrode area, C Li^+ concentration, v scan rate, T temperature, and R gas constant (Pan et al., 2019). The results are shown in Table 4.2.

Table 4.2 Diffusion coefficient D of Li^+ ions for WO_3 thin films with different thicknesses

Sample	Cathodic current	Anodic current	Diffusion coefficient	
	J_{pc} (A)	J_{pa} (A)	$D_{cathodic}$ (cm^2s^{-1})	D_{anodic} (cm^2s^{-1})
WO_3 -1	-6.50×10^{-3}	5.75×10^{-3}	6.49×10^{-10}	5.077×10^{-10}
WO_3 -2	-5.80×10^{-3}	5.49×10^{-3}	5.16×10^{-10}	4.63×10^{-10}
WO_3 -3	-6.36×10^{-3}	5.96×10^{-3}	6.22×10^{-10}	5.46×10^{-10}
WO_3 -4	-6.98×10^{-3}	6.65×10^{-3}	7.50×10^{-10}	6.80×10^{-10}

4.1.3 Optical Properties

Ex-situ measurements of optical transmittance of colored and bleached state in the UV-VIS-NIR range for electrochromic WO_3 thin films in 1M LiClO_4 have been measured. These measurements were recorded when the current density was zero and the cycle was to be reversed at the fully colored or bleached state after 5 cycles of CV. There are an increase in the optical modulation (ΔT) in the visible region when the thickness of the investigated samples is increased (Figure 4.6). The results of optical modulation, optical density and color efficiency at 550 nm of the sputtered WO_3 thin films are shown in Table 4.3.

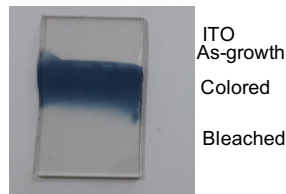


Figure 4.5 Coloration states of a DC magnetron sputtered WO_3 thin film on ITO/Glass (Personal archive, 2020)

Table 4.3 Transmittance modulation, optical density and color efficiency at 550 nm of WO₃ films with different thicknesses

Sample	Bleached (%)	Colored (%)	ΔT (%)	Optical Density (ΔOD)	Color efficiency ($\text{cm}^2 \text{C}^{-1}$)
WO ₃ -1	77.99	31.40	46.59	0.91	47.64
WO ₃ -2	79.06	22.04	57.02	1.27	68.22
WO ₃ -3	77.42	11.68	65.74	1.89	87.66
WO ₃ -4	77.77	11.99	65.78	1.86	78.16

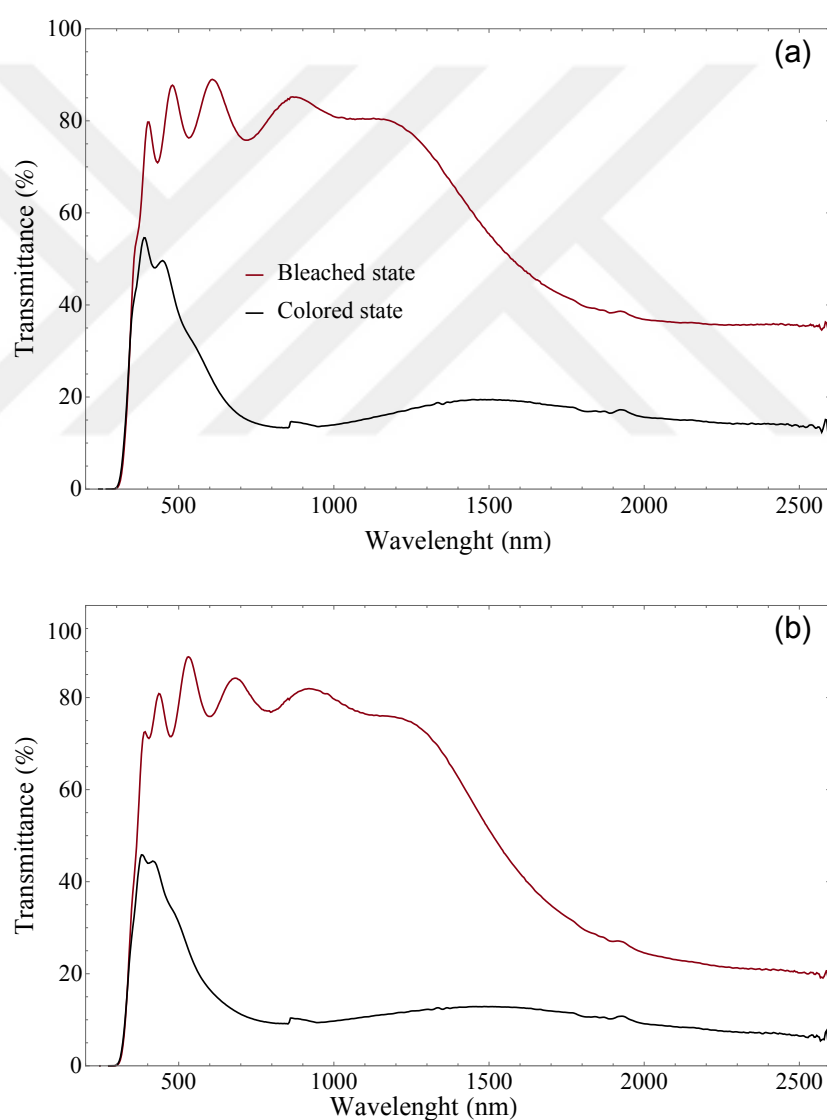


Figure 4.6 Transmittance in the the $200 < \lambda < 2600$ wavelength interval of the electrochromic WO₃ thin films with different thickness (a) WO₃-1, (b) WO₃-2, (c) WO₃-3 and (d) WO₃-4 immersed in 1 M LiClO₄-PC electrolyte

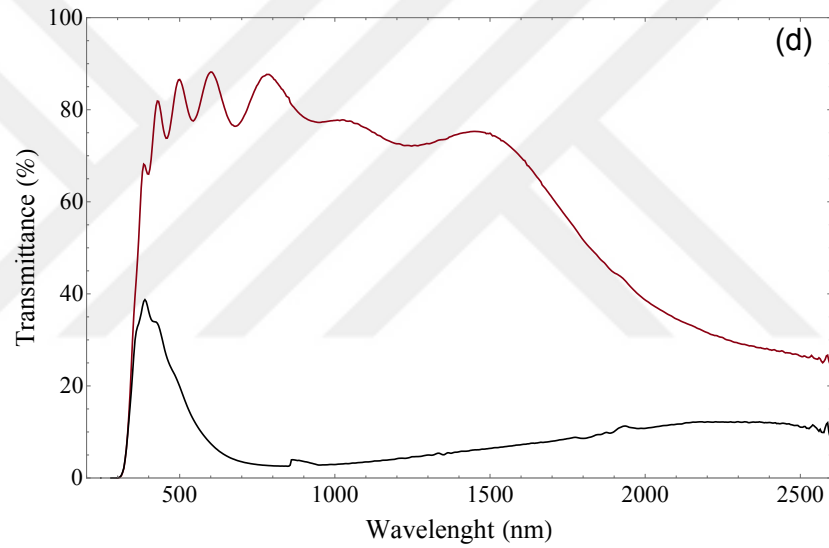
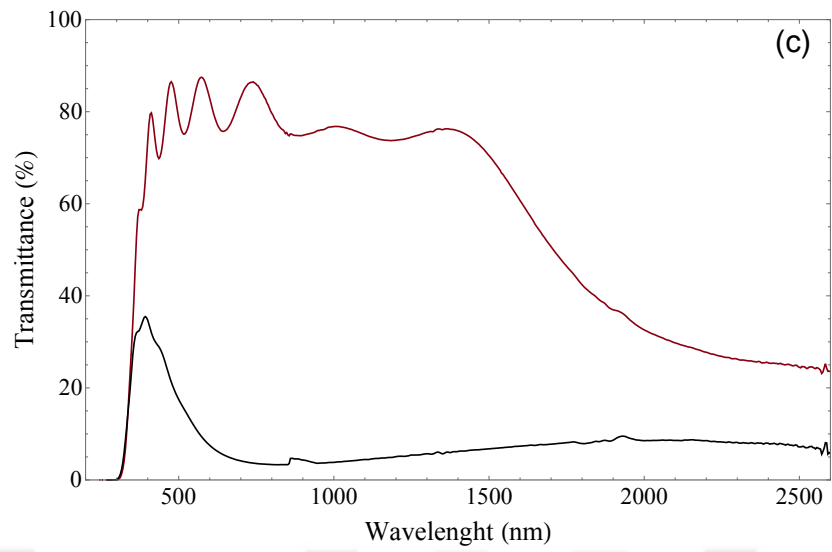


Figure 4.6 continues

Figure 4.7 shows ex-situ colour shift of WO_3 samples deposited by off-axis DC magnetron sputtering, obtained from the transmittance in the visible range.

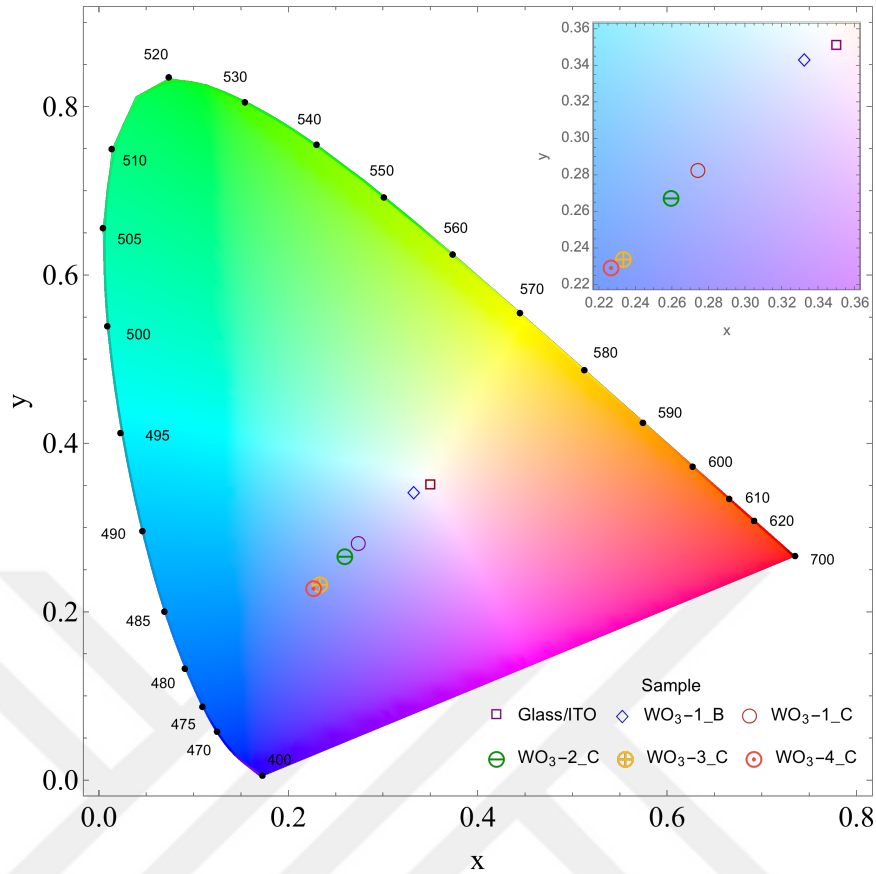


Figure 4.7 CIE 1931 chromaticity diagram. Shift of different blue tonalities can be observed for WO_3 thin film samples with different thicknesses in the colored state

4.2 Nickel Oxide

4.2.1 Physical Properties

It is known that as-deposited electrochromic NiO_x thin films show an intermediate optical state between the bleached and colored state which is irreversible under insertion/extraction of ions. In this work electrochromic NiO_x thin film were obtained. Table 4.4 shows the thickness corresponding to the different deposition times, determined by surface profilometry.

Table 4.4 Thickness of NiO_x thin films with different deposition times on the glass/ITO substrates

Sample	Sputtering Time (min)	Thickness (nm)
NiO_x -1	40	194.79
NiO_x -2	50	256.02
NiO_x -3	60	340.86
NiO_x -4	70	399.33

4.2.2 Electrochemical Properties

The NiO_x thin film series were electrochemically cycled in 1M LiClO_4 -PC in a potential range between -0.5 and 1.5V vs Ag/AgCl for electrochemical testing. Figure 4.8 shows the voltammogram at the scan rate of 100 mV/s. As is observed similarly to the a- WO_3 investigated in this thesis, the higher the film thicknesses is, the more current flows through the thin film, and thus the higher anodic and cathodic peak current intensities. So charge capacity depends strongly on sample thickness and also greater amount of Li^+ ion insertion increase when potential range is increased (Figure 4.9).

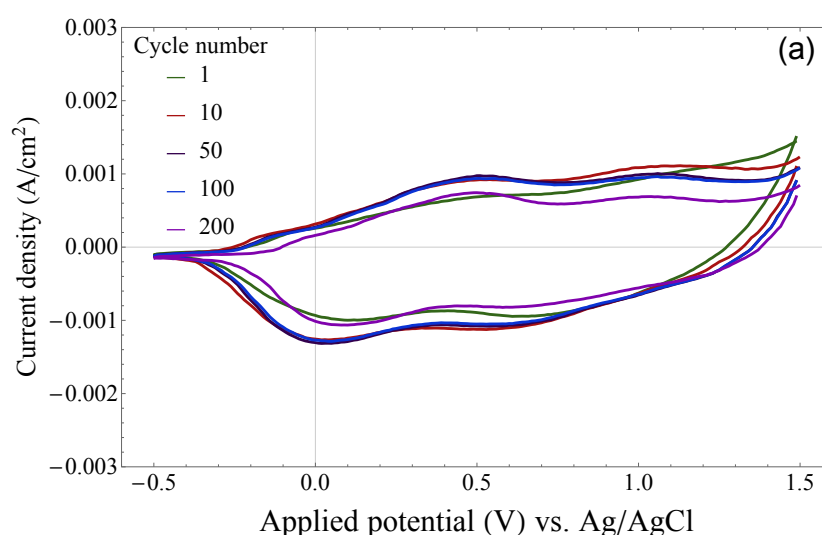


Figure 4.8 Evolution of the CVs at the cycle 1, 10, 50, 100 and 200 with different thicknesses (a) NiO_x -1, (b) NiO_x -2, (c) NiO_x -3 and (d) NiO_x -4 immersed in 1 M LiClO_4 -PC electrolyte

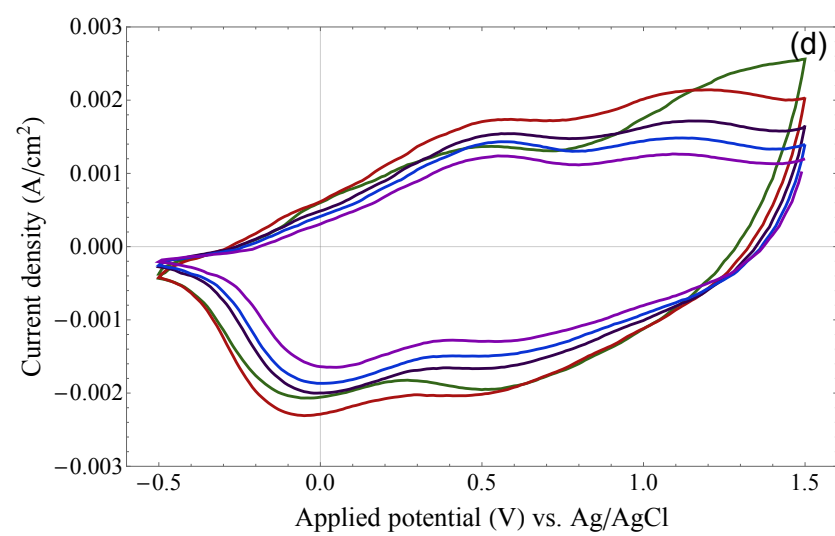
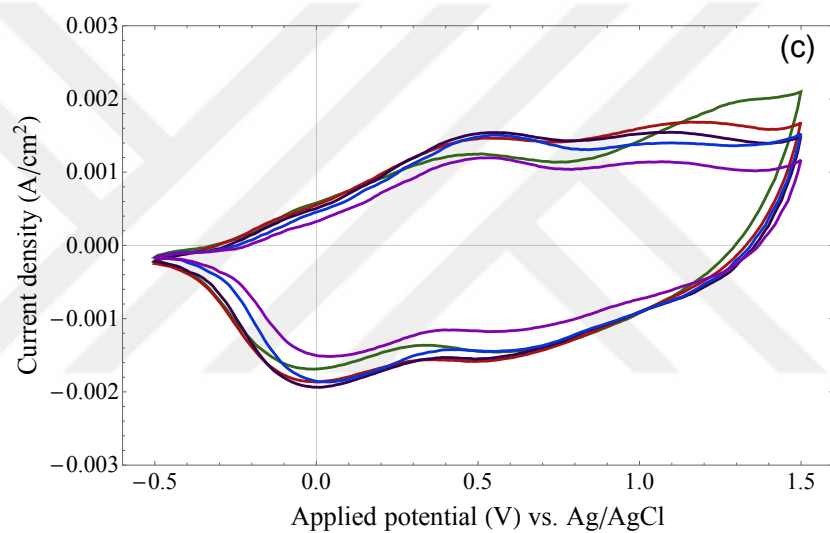
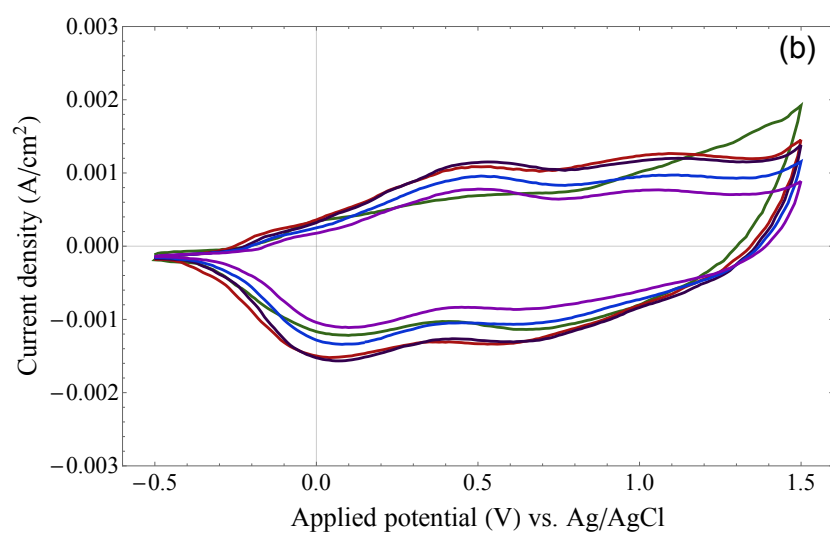


Figure 4.8 continues

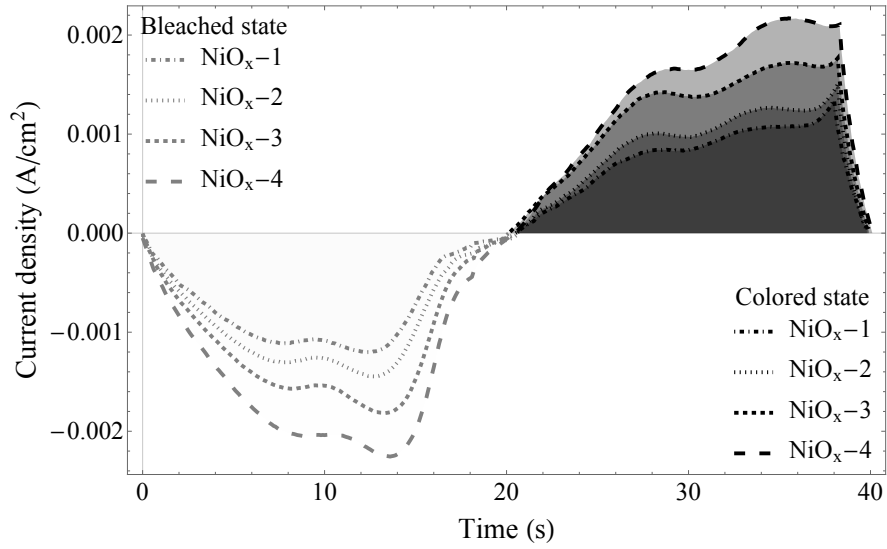


Figure 4.9 Evolution of the current density basing on the 20 time CV measurement at 100 mV/s with different thicknesses of NiO_x thin films

The diffusion coefficient D of Li^+ ions in the NiO_x thin films was obtained from the Randles-Servick equation (4.1). The results are shown in Table 4.5.

Table 4.5 Diffusion coefficient D of Li^+ ions for NiO_x thin films with different thicknesses

Sample	Cathodic current	Anodic current	Diffusion coefficient	
	J_{pc}	J_{pa}	$D_{cathodic}$	D_{anodic}
	(A)	(A)	(cm^2s^{-1})	(cm^2s^{-1})
NiO_x -1	-1.20×10^{-3}	1.34×10^{-3}	2.22×10^{-11}	2.76×10^{-11}
NiO_x -2	-1.44×10^{-3}	1.50×10^{-3}	3.21×10^{-11}	3.47×10^{-11}
NiO_x -3	-1.81×10^{-3}	1.76×10^{-3}	5.07×10^{-11}	4.79×10^{-11}
NiO_x -4	-2.25×10^{-3}	2.16×10^{-3}	7.81×10^{-11}	7.22×10^{-11}

4.2.3 Optical Properties

Ex-situ measurements of optical transmission in the bleached and colored states in the UV-VIS-NIR range for the anodic coloring NiO_x thin films cycled in 1M LiClO_4 have been measured. These measurements were recorded when the current density was zero

and the cycle was to be reversed at the fully colored or bleached state after 15 cycles of CV to ensure the activation of the EC properties of the film. There are no significant change in optical transmittance from the initial state to the bleached one. However there are significant increase in the optical modulation (ΔT) between the colored state and the bleached one in the visible region when the thickness of the films are increased (Figure 4.11). The results of optical modulation, optical density and color efficiency at 550 nm of the sputtered NiO_x thin films are shown in Table 4.6.

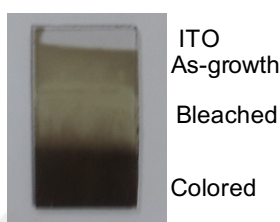


Figure 4.10 Coloration states of a DC magnetron sputtered NiO_x thin film on ITO/Glass (Personal archive, 2020)

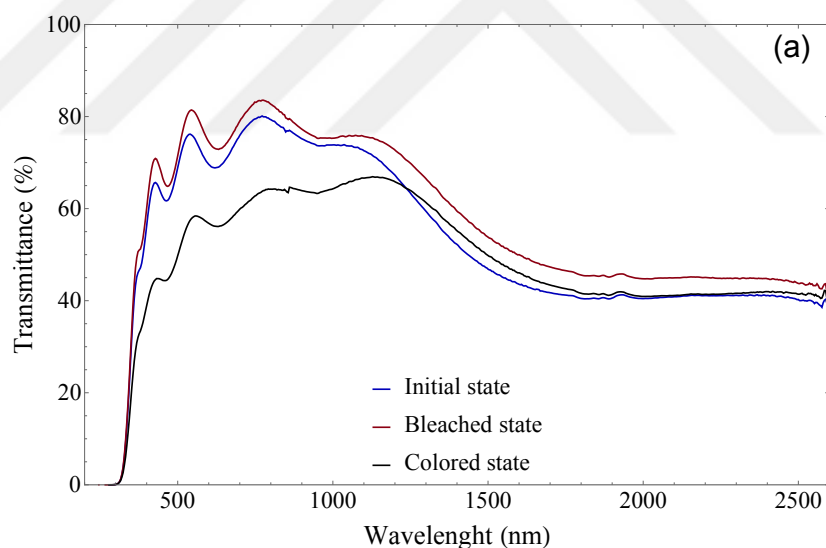


Figure 4.11 Transmittance in the the $200 < \lambda < 2600$ wavelength interval of the electrochromic WO_3 thin films with different thickness (a) NiO_x -1, (b) NiO_x -2, (c) NiO_x -3 and (d) NiO_x -4 immersed in 1 M LiClO_4 -PC electrolyte

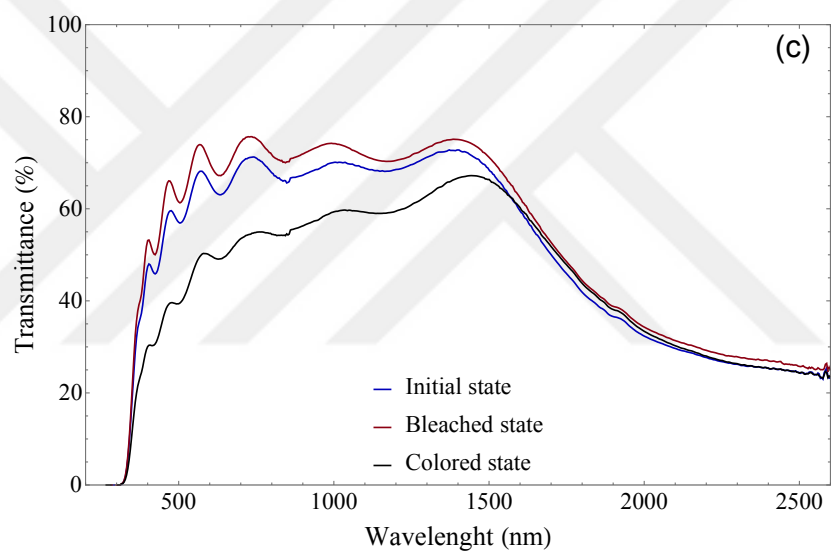
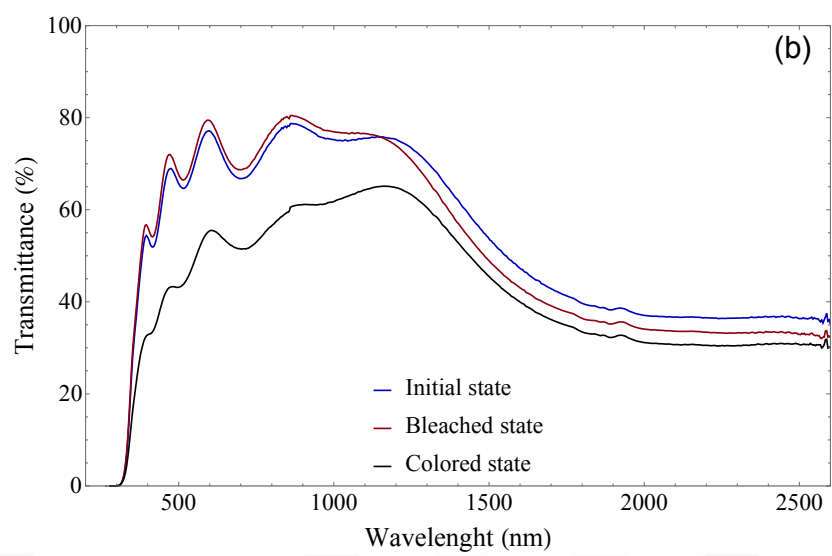


Figure 4.11 continues

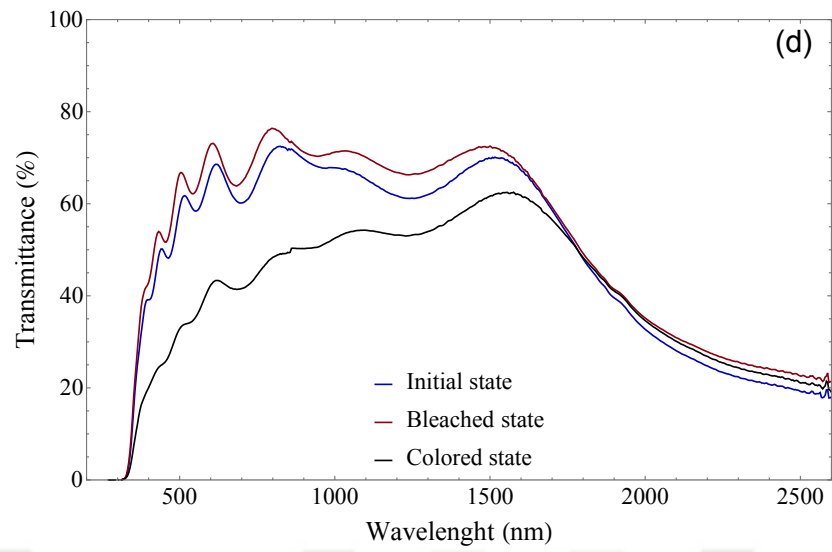


Figure 4.11 continues

Figure 4.12 shows ex-situ colour shift of NiO_x samples deposited by off-axis DC magnetron sputtering, obtained from the transmittance in the visible range.

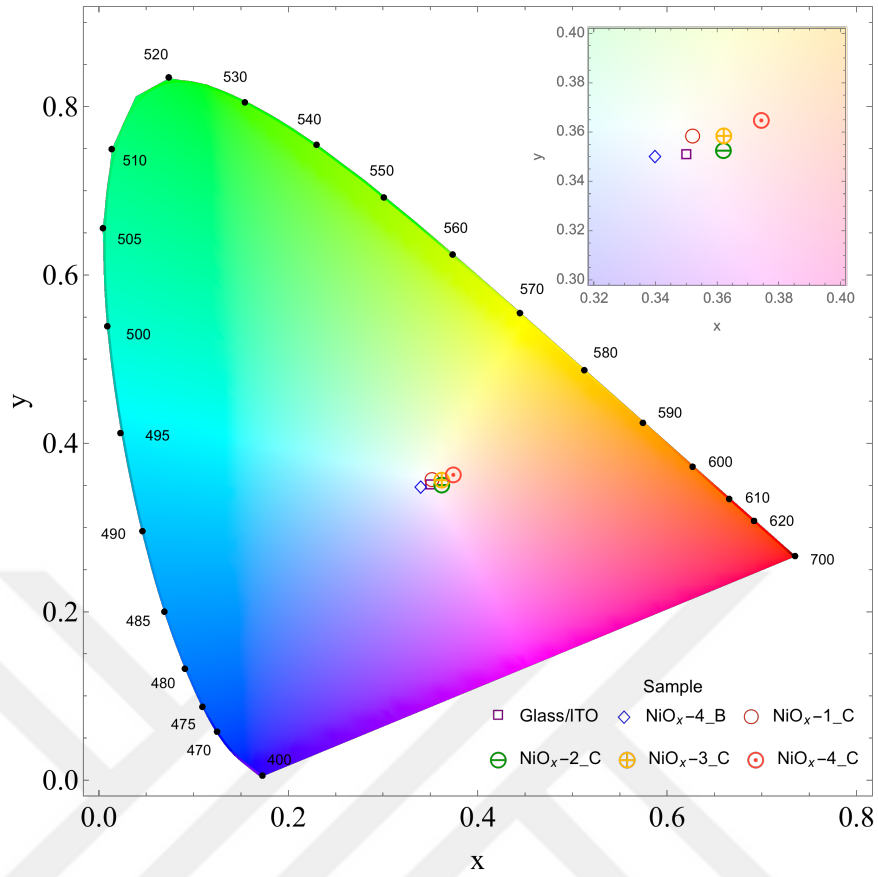


Figure 4.12 CIE 1931 chromaticity diagram. Shift of color can be observed for NiO_x thin film samples with different thicknesses in the colored state

Table 4.6 Transmittance modulation, optical density and color efficiency of NiO_x films with different thicknesses

Sample	Bleached (%)	Colored (%)	ΔT (%)	Optical density (ΔOD)	Color efficiency ($\text{cm}^2 \text{C}^{-1}$)
NiO_x -1	81.22	58.17	23.05	0.33	67.39
NiO_x -2	71.95	48.67	23.28	0.39	65.61
NiO_x -3	71.83	47.04	24.79	0.42	57.01
NiO_x -4	69.72	35.22	34.50	0.68	71.42

4.3 Assembling of the ECD

First, the WO_3 (or NiO_x) thin films were deposited on ITO/Glass, then 1 mm thick double sided band was used as spacer between the two electrodes. Then due to its higher optical modulation in comparison with the other samples, NiO_x -4 was employed as secondary electrochromic layer for the ECD in combination with the others WO_3 samples. The electrodes were attached and the ECD was sealed with epoxy. Subsequently, 1 M $\text{LiClO}_4 + \text{PC}$ liquid electrolyte was injected into the 1 mm-thick space between the electrodes by using a syringe as is shown in Figure 4.13.

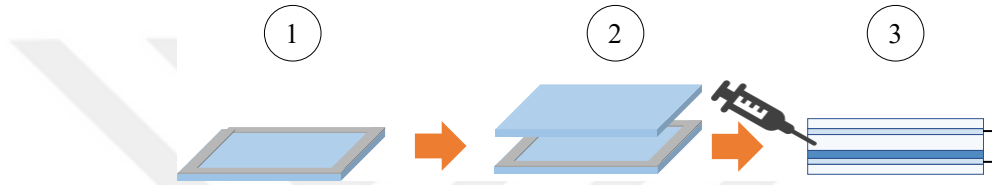


Figure 4.13 Assembly of an ECD

The configurations of the ECD was as follows : NiO_x -4// WO_3 -1, NiO_x -4// WO_3 -2, NiO_x -4// WO_3 -3, NiO_x -4// WO_3 -4. For electrochromic testing the ECDs prototypes were cycled by using chrono amperometry technique, giving 10 s for coloring/bleaching change. Table 4.7 shows the optical modulation for the different ECDs. In Figure 4.14 is shown the optical modulations at different applied potentials, where an increase in the optical modulation can be observed when the potential is increased. In Figure 4.15 is observed the evolution upon cycling in the colored and bleached states of the ECDs at 550nm over 300 cycles. As can be observed in Figure 4.16, the optical modulation increase to its maximum at approximately the cycle number 100 for all the ECDs, then a decreasing in the optical modulation is observed. This can be explained because of ion trapping in thicker WO_3 samples. Then ECD-4 sample was cycled up to 1000 cycles as can be observed in Figure 4.17 there is no significant decreasing in its optical modulation when -1.5/1.5 V is applied.

Table 4.7 Transmittance modulation, optical density and color efficiency of the ECDs

Sample	Bleached (%)	Colored (%)	ΔT (%)	Optical density (ΔOD)	Color efficiency ($\text{cm}^2 \text{C}^{-1}$)
ECD-1	73.96	20.39	53.57	1.28	180.31
ECD-2	70.82	22.66	48.16	1.13	179.89
ECD-3	70.46	24.85	45.61	1.04	181.76
ECD-4	72.52	26.47	46.05	1.00	186.29

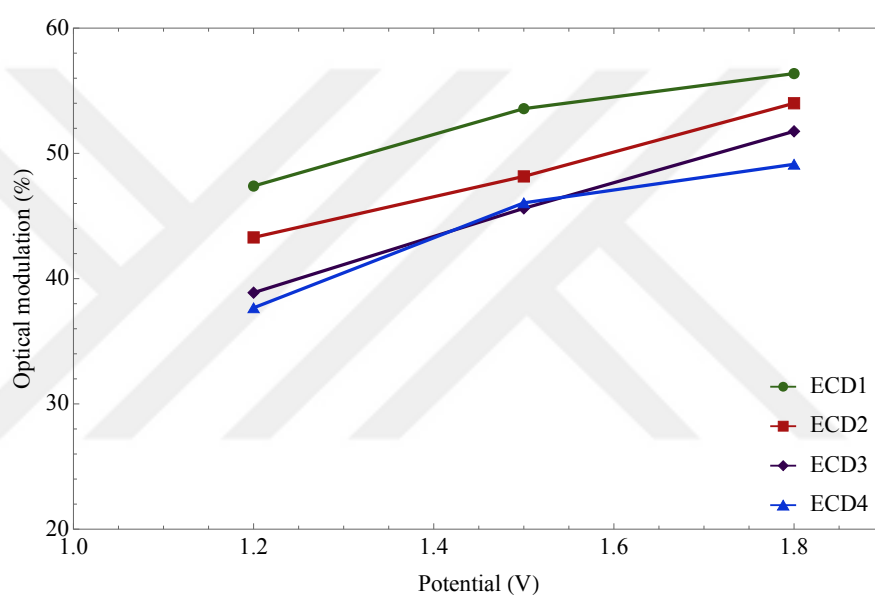


Figure 4.14 Optical modulation of all ECDs by applying -1.2/1.2, -1.5/1.5, and -1.8/1.8. This figure shows an increasing of optical modulation when the applied potential is increased

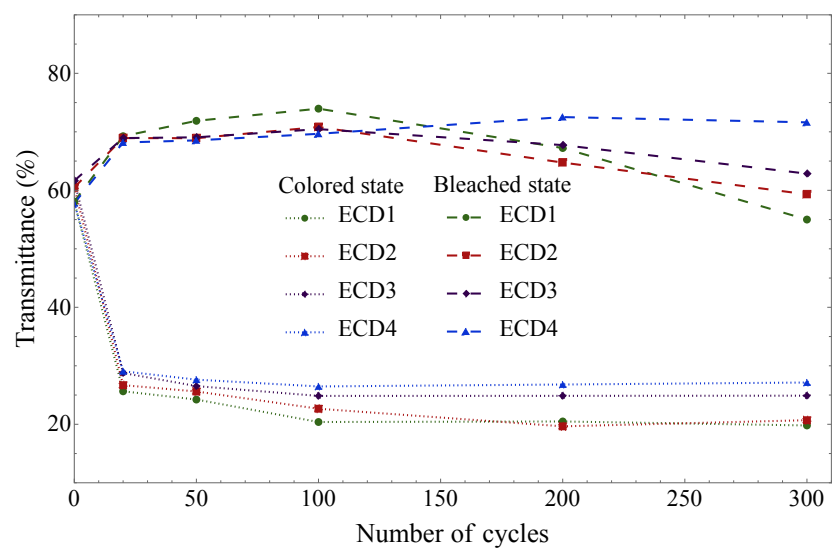


Figure 4.15 Evolution of the bleached and colored state of the ECDs at 550nm over 300 cycles by applying ± 1.5 V with CA technique

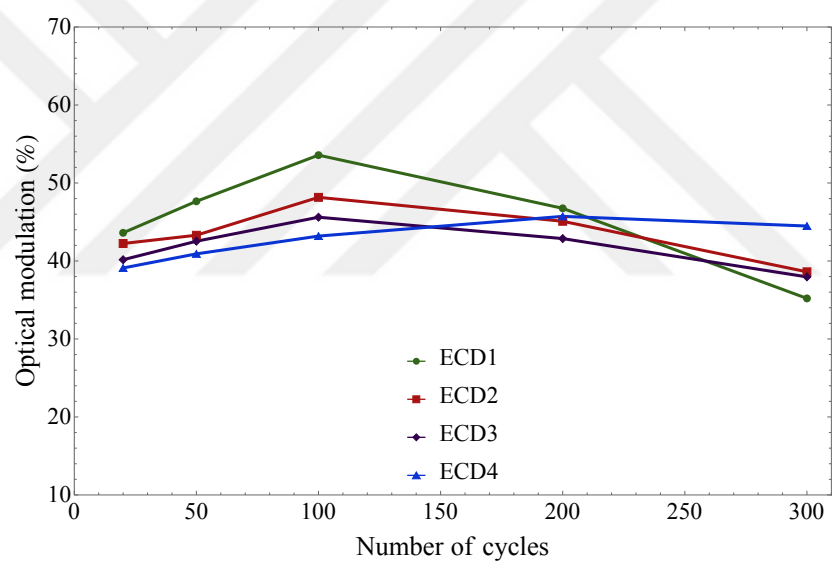


Figure 4.16 Evolution of the transmittance modulation of the ECDs at 550nm over 300 cycles by applying ± 1.5 V with CA technique

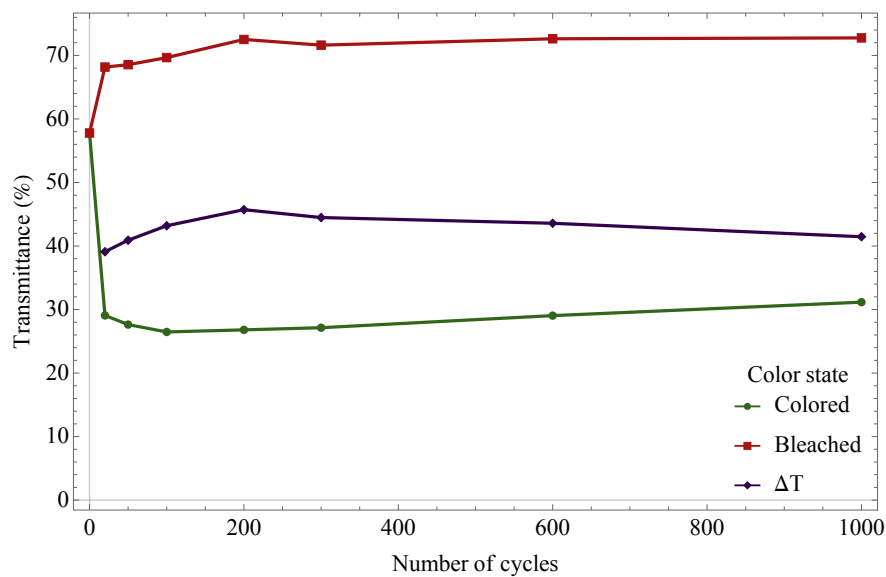


Figure 4.17 ECD-4 cycled 1000 times by applying -1.5/1.5 V. No significant lose in its optical modulation is observed

Figure 4.18 shows CA measurement of ECD-4 for 5 cycles where current density response can be observed when the potential is changed.

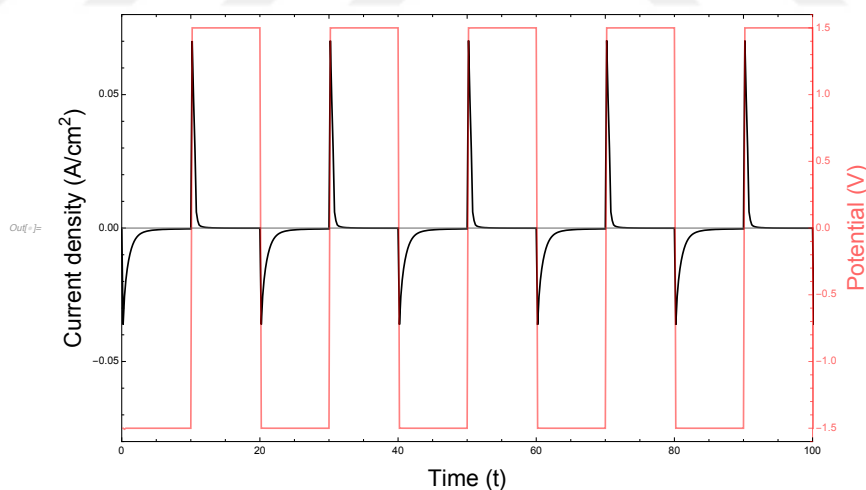


Figure 4.18 Chronoamperometry of ECD-4 for 5 cycles

Finally, a comparison with previous works where WO_3 and NiO_x electrochromic thin films are employed in ECDs is shown in Table 4.8. The coloring and bleaching time for the ECD-4 was obtained by taking a video of the device during the CA measurement

and then by using a video editor that shows 23 frames per second. Then by employing this method, an approximation for the bleaching and coloring times was obtained.



Table 4.8 Comparison of ECDs based on WO_3/NiO_x thin films with our results and literature

Device	Deposition Method	Potential V_C/V_B	ΔT (%)	t_C/t_B (s)	λ_T (nm)	Ref
Glass/ITO/ NiO_x /polyelectrolyte/ WO_3 /ITO/Glass	reactive DC magnetron	-2.5/2.5	55	10/20	550	J. Zhang et al., 2009
Glass/ITO/ NiO_x / LiClO_4 - PC/ WO_3 /ITO/Glass	chemical bath deposition (NiO_x)/ electrodeposition (WO_3)	-2.5/2.5	84	1.76/1.54	550	Huang et al., 2011
Glass/ITO/ NiO_x / LiTaO_3 / WO_3 /ITO	reactive DC magnetron	-5/5	67	85/42	550	Song et al., 2015
Glass/ITO/ WO_3 / LiClO_4 -PC- PMMA/ NiO_x /ITO/Glass	reactive DC magnetron	-1.8/1.8	51.7	5/2	550	Q. Liu et al., 2016
Glass/ITO/ NiO_x / LiNbO_3 / Ta_2O_5 / WO_3 /ITO	reactive DC magnetron	-1.5/0.5	20.3	–	550	Liu et al., 2018
Glass/ITO/ NiO_x / Ta_2O_5 / LiNbO_3 / Ta_2O_5 / WO_3 /ITO	reactive DC magnetron	-2.0/1.8	52.5	21/21	550	Liu et al., 2018
Glass/ITO/ NiO_x / Ta_2O_5 / Ta_2O_5 - PC- PMMA/ WO_3 /ITO/Glass	Photodeposition	-2.1/2.1	60	4/6	633	Cheng et al., 2018
Glass/ITO/ NiO_x / Ta_2O_5 / WO_3 /ITO	reactive DC magnetron	-1.8/1.8	70.9	13/2	600	Pan et al., 2019
Glass/ITO/ WO_3 / LiClO_4 -PC/ NiO /ITO/Glass	cathodic arc plasma	-1.5/0.8	46	3.1/4.6	633	Chen et al., 2020
Glass/ITO/ NiO / Ta_2O_5 / Li/WO_3 /ITO	e-beam	-2.5/2.5	52.6	62.5/33.4	550	Li et al., 2020
Glass/ITO/ WO_3 / LiClO_4 -PC/ NiO /ITO/Glass	off-axis reactive DC magnetron sputtering	-1.5/1.5	46	$\sim 3/\sim 1$	550	This work

CHAPTER FIVE

CONCLUSIONS

In this work electrochromic the metal oxides WO_3 and NiO_x were deposited satisfactorily by reactive DC magnetron sputtering in an Ar/O_2 mixing gas by using off-axis sputtering technique during the deposition process. From XRD an amorphous structure of the WO_3 thin films can be deduce, since there was not external thermal energy provided. A porous structure was deduced from the color change as consequence of the ion insertion/extraction in the cyclic voltammetry. To determine the performance of the electrochromic thin film series a prototype ECDs was assembled. The results show that the WO_3 sample with a thickness about ~ 300 nm in combination with a NiO_x sample with a thickness of ~ 400 nm show a good optical modulation over 1000 cycles and also with fast switching time by applying $-1.5/1.5$ V in a chronoamperometry measurement.

The experiments also show that WO_3 thin films with higher thicknesses in combination with the 400 nm-thick NiO_x result in ion trapping, it means that Li^+ ions get trapped into the WO_3 thin film structure and a reversible change in their optical properties from a colored to a transparent state as well as its optical modulation decreased.

In general the results obtained in this thesis show that off-axis sputtering technique and slow deposition rates have influence in the formation of a- WO_3 and NiO_x thin films and the diffusion of ions during the coloration-bleaching process. Also off-axis sputtering technique allows us to deposit porous thin films at lower pressures protecting the substrate and the thin films during the growing process from the bombardment of high-energy particle/atoms ejected from the target, giving low defect in the as-deposited thin films, resulting in a good performance of the magnetron sputtered thin films for electrochromic device applications.

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