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Dynamic Electrochromic Antireflective Coatings for Ophthalmic Applications

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Mémoire présenté en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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présenté par **Martin CROUAN**

en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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RÉSUMÉ

Un verre dynamique, qui peut passer d'un état transparent à un état coloré, présente un intérêt potentiel pour de nombreuses applications dans notre vie quotidienne. Différentes sources d'énergie peuvent entrer en jeu, en fonction des stimuli requis à l'activation du produit. Les matériaux électrochromiques gagnent en popularité dans l'industrie en raison de leur contrôlabilité, de leur adaptation aux besoins immédiats des utilisateurs, de leur réversibilité et de leur faible consommation d'énergie. L'utilisation de ces matériaux dits "intelligents" dans les verres architecturaux semble déjà très prometteuse en matière d'amélioration de l'efficacité énergétique des bâtiments. Cependant, ils peuvent également améliorer le confort de l'utilisateur dans des produits déjà existants, tels que les hublots d'avion ou les rétroviseurs de voiture.

Dans ce projet, je me suis concentré spécifiquement sur l'utilisation des matériaux électrochromiques pour les applications ophtalmiques. Ces matériaux permettent aux utilisateurs de contrôler la teinte du verre en fonction des conditions d'éclairage. À cette fin, des dispositifs électrochromiques entièrement basés sur des couches minces peuvent être développés pour s'aligner sur les techniques de dépôt déjà utilisées dans l'industrie. En particulier, le WO_3 et le NiO ont été étudiés en tant que matériaux cathodiques et anodiques, respectivement, en raison de leurs comportements électrochromiques complémentaires; le WO_3 se colore lors de l'insertion tandis que le NiO se colore lors de l'extraction d'ions dans leurs microstructures et *vice-versa*. L'objectif principal de ce projet vise donc à obtenir un dispositif électrochromique par couches minces qui démontre une grande transparence et une faible réflexion ($\Delta R_{lum} < 2.5\%$) dans l'état transparent, tout en montrant une augmentation de 10% de la réflexion lors de la coloration.

Une procédure de nettoyage rigoureuse a donc été mise au point pour minimiser la présence de particules sur le substrat, qui sont une source courante de défauts se propageant jusqu'à la surface des dispositifs, entraînant ainsi des courts-circuits. En outre, les matériaux ont été déposés dans la zone centrale du substrat, en omettant les bords, afin de garantir une meilleure performance des dispositifs. Grâce à une méthodologie de fabrication optimisée, la perte de couleur immédiate a été éliminée avec succès dans tous les dispositifs fabriqués. Chaque matériau a été optimisé pour garantir une grande porosité, ce qui est crucial pour obtenir d'excellentes performances électrochromiques. Cependant, alors que le WO_3 et le NiO sont connus pour présenter une grande

modulation de la transmission et de l'absorption, la réflexion lors de la coloration n'a montré que des changements mineurs, parfois même une diminution. Pour résoudre ce problème et atteindre l'objectif d'une augmentation de 10% de la réflexion, une nouvelle approche a été développée, basée sur des miroirs de Bragg alternant des couches de WO_3 et d'ITO, au lieu d'une seule couche de WO_3 dans le dispositif. Ce concept a donné des résultats prometteurs en passant d'un état transparent et antireflet à un état coloré présentant un effet miroir. Bien que la modulation obtenue soit inférieure à celle attendue par la modélisation (de $R_{lum} = 1,4\%$ à $R_{lum} = 8,9\%$ comparé à la modélisation qui prédisait un changement de $R_{lum} = 0,6\%$ à $R_{lum} = 12,2\%$), elle représente néanmoins une amélioration significative par rapport à l'architecture standard sans les miroirs de Bragg. Cependant, il a été démontré que si l'on ne cherchait pas à obtenir un état antireflet, les dispositifs étaient capables de présenter de meilleures modulations de réflexion. Enfin, les tests de durabilité effectués sur les dispositifs ont montré une dégradation au fil du temps, principalement due au piégeage des charges et aux réactions secondaires entre les protons et les matériaux électrochromiques.

ABSTRACT

Dynamic glass, which can switch between bleached and colored states, is of potential interest for numerous applications in our daily lives. Various energy sources can come into play, depending on the stimuli required to activate the product. As such, electrochromic materials are gaining in popularity in the industry due to their controllability, adapting to the users' immediate needs, reversibility, and low energy consumption. The implementation of such "smart" materials in architectural glass has shown promising results in improving energy efficiency in buildings. However, they can also enhance user comfort in existing products, such as aircraft windows or car rear-view mirrors.

In this project, I focused specifically on exploring the applicability of electrochromic materials in ophthalmic applications. These materials offer the possibility for users to control the tint of the glass based on lighting conditions. To this end, electrochromic devices based entirely on thin films can be developed to align with established deposition techniques utilized in the industry. For this purpose, WO_3 and NiO were investigated as cathodic and anodic materials, respectively, due to their complementary electrochromic behavior; WO_3 colors upon insertion whereas NiO colors upon extraction of ions in their respective microstructures and *vice-versa*. The main goal of this project was to fabricate an all-solid-state electrochromic device that reaches high transparency and low reflection ($\Delta R_{lum} < 2.5\%$) in the bleached state, while showing an increase of 10% in reflection upon coloration.

A rigorous cleaning procedure was thus developed to minimize the presence of particles on the substrate, which are a common source of defects that propagate to the surface of the devices, resulting in short circuits. In addition, the materials were deposited in the central area of the substrate, omitting the edges, to ensure a better performance of the devices. Through an optimized fabrication methodology, the obvious self-bleaching was successfully eliminated in all fabricated devices. Each material was optimized to ensure a sufficient amount of porosity, which is crucial for excellent electrochromic performance. However, while WO_3 and NiO are known for exhibiting significant transmission and absorption modulation, the reflection upon coloration showed only minor changes, sometimes even decreasing. To address this and achieve the targeted 10% increase in reflection, a new approach was implemented based on Bragg mirrors consisting of alternating

WO₃ and ITO layers, instead of the typical single WO₃ layer in the device. This design demonstrated promising results by transitioning from an anti-reflective bleached state to a mirror-like colored state. Although the achieved modulation was lower than expected by modeling (from $R_{lum} = 1.4\%$ to $R_{lum} = 8.9\%$ compared to the modeled $R_{lum} = 0.6\%$ to $R_{lum} = 12.2\%$), it still represented a significant improvement when compared to the standard architecture without the Bragg mirrors. Nevertheless, if anti-reflective properties are not sought, devices with significantly higher reflection modulations can be designed and fabricated. Finally, the durability tests performed on the devices showed degradation over time, mainly due to charge trapping and side reactions between the protons and the electrochromic materials.

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbols:

A	Absorption
α	Alpha phase
T_a	Ambient temperature
ψ	Amplitude ratio between the polarizations
i_p	Anodic current
V	Applied potential
N_A	Avogadro constant
β	Beta phase
i_b	Bleaching current
i_c	Coloration current
η	Coloration efficiency
C_0	Concentration of the electrolyte
ρ_M	Density of the studied film
D_i	Diffusion coefficient of ions
e^-	Electron
e	Elementary charge
k	Extinction coefficient
F	Faraday constant
γ	Gamma phase
T^*	Generalized temperature
I	Illuminant

Δt	Increment of time
x	Intercalation ratio
M^+	Ion taking part in the electrochromic reaction
μ_{H^+}	Ionic mobility
T_{lum}	Luminous transmission
R_{lum}	Luminous reflection
R_{lum_B}	Luminous reflection in the bleached state
R_{lum_C}	Luminous reflection in the colored state
ρ_b	Material's bulk density
M	Molar mass of the studied film
t^*	Net thickness
E^*	Normalized energy of the ions flux
n_e	Number of electrons
Q_i	Number of inserted charges
r_p	p-polarization of the reflection in the plane of incidence of the light
Δ	Phase delay between the polarizations
$\bar{y}$	Photopic luminous efficiency curve
R	Reflection
n	Refractive index
n_b	Refractive index of the chosen material in bulk form
n_f	Refractive index of the chosen material in thin film form
ε	Relative dielectric permittivity
ρ	Resistivity

τ	Response time
r_s	s-polarization of the reflection perpendicular to the plane of incidence of the light
v	Scan rate
S	Scattering
C_s	Solution concentration
d	Thickness of the studied film
t	Time
T	Transmission
T_b	Transmission in the bleached state
T_c	Transmission in the colored state
R_g	Universal gas constant
p_{H^+}	Volume charge density of the protons
λ	Wavelength
A_{WE}	Working electrode area

Abbreviations:

AR	Anti-reflective
ASSD	All-solid-state device
CE	Counter electrode
CIE	International Commission on Illumination
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
DC	Direct current

DI	De-ionized
EC	Electrochromic
EMA	Effective medium approximation
FCSEL	Functional Coating and Surface Engineering Laboratory
IR	Infrared
LC	Liquid crystal
MS	Magnetron sputtering
MSE	Mean square error
OCP	Open-circuit potential
OIC	Optical Interference Coatings
PET	Polyethylene terephthalate
PVD	Physical vapor deposition
RE	Reference electrode
RF	Radiofrequency
SCE	Saturated calomel electrode
SPD	Suspended particle device
SZD	Structure zone diagram
TCE	Transparent conductive electrode
UMA	Universal measurement accessory
UV	Ultraviolet

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CHAPTER 1 INTRODUCTION

1.1 Dynamic coatings – Towards advanced ophthalmic applications

1.1.1 Interest in dynamic coatings for the eyewear industry

According to a 2022 report, nearly 79% of the adult population of the United States is using visual correction, with three out of four people using prescription glasses and sunglasses [1]. Combining the functionality of clear and tinted glasses into a single pair could have numerous benefits. It would reduce the amount of material needed for production and save consumers money. One already implemented solution which is available on the market is the use of dynamic – or smart – lenses. They are typically based on photochromic materials which can change from a tinted or dark state when exposed to ultraviolet (UV) rays from the sun to a transparent state indoors. This technology was first introduced on the market in 1991, and now, several important eyewear companies such as EssilorLuxottica and Carl Zeiss A.G. offer such smart lenses [2].

Although photochromic lenses offer many benefits, they do have some drawbacks for everyday use. For instance, they can lose their effectiveness when inside a car, as many car windows block UV rays, limiting the user's control over the tint of their glasses. Additionally, the time it takes for the lenses to clear and darken is sometimes quite long (several minutes), and, over time, the glasses may retain a certain tint and no longer become fully transparent. Basically, they are adaptable to the user's needs, but not controllable. Therefore, several studies have been carried out to mitigate the drawbacks of photochromic glasses.

A solution that has strongly been considered is the use of electrochromic (EC) glasses, which allow a change between a transparent state and a colored state upon the application of a small electric current in a controllable and reversible manner. This technology offers users a greater level of control, allowing them to adjust the tint according to the duration of the current application. This would enable a single pair of glasses to possess different tint levels, depending on the amount of light transmitted or absorbed through the lenses. The tint could range from a lighter shade for aesthetic purposes, to a darker coloration for higher light exposures, for instance in a mountainous environment, making it possible to achieve all sunglass categories in a single pair [3].

1.1.2 Growing market for chromogenic glass

Photochromic and EC coatings are part of a larger family of materials defined as chromogenic which allow a reversible transition between colored and transparent states in response to an external stimulus as summarized in Table 1-1. These materials are divided into two subgroups: adaptive materials, which respond to environmental stimuli such as light (photochromic) or temperature (thermochromic); and controllable materials, which can be controlled by the user through the presence of a gas (gasochromic), an electric current (electrochromic) or the application of a macroscopic pressure (piezochromic) [4].

Table 1-1: Summary of important chromogenic categories and examples of such materials.

	Category	External stimuli	Examples
Adaptive	Photochromic	Light	AgCl, AgBr
	Thermochromic	Temperature	VO ₂
Controllable	Gasochromic	Gas	WO ₃ , MoO ₃
	Piezochromic	Pressure	Spiropyrans
	Electrochromic (EC)	Electric field	NiO, WO₃, Prussian blue

Chromogenic materials have become a topic of great interest in recent years due to their potential application in a wide range of fields, such as smart windows, information displays, and the automotive and eyewear industries [5]. Due to their controllable behavior, low energy consumption, and high durability, the EC materials market is expanding with a current market value estimate of 2.43 billion dollars and an expected average annual growth rate of 16.5% until 2029 [6]. Their ability to modulate transmission and reflection over the visible and infrared (IR) spectra opens up new opportunities that are already being investigated. For example, Gentex

Corporation has developed dimmable glass for rear-view mirrors which modulate its reflection to reduce glare from the environment, specifically to eliminate high intensity reflections from the surrounding cars' headlamps. They also developed an EC product for airplane windows (implemented in the Boeing 787) to control the amount of light passing through to maintain the user's safety and comfort. However, the current main application of EC materials is smart windows where the owner or an automated control software controls the glare and the amount of heat from the sun's irradiation coming inside a building. This technology has tremendous potential for energy conservation, as buildings are responsible for 30% of global CO₂ emissions, primarily due to their low insulation behavior when it comes to heating and cooling [7]. The dynamic behavior of EC devices allows them to efficiently transmit the heat from the sun's near-IR irradiation into buildings during cold weather while absorbing it during warmer seasons. In the latter scenario, however, the EC device needs to be paired with a low emissivity coating to reflect higher-wavelength IR radiation that are re-emitted by the EC device. The incorporation of EC materials in architectural windows could, therefore, lead to significantly reducing the demand for heating and air conditioning, leading to cost and energy savings.

In addition to EC devices, other technologies are already used in smart windows on the market which are also using an electric stimulus. These include suspended particle devices (SPD) and liquid crystals (LC). The principle of SPD is that suspended particles are arranged randomly in the absence of a current, leading to the absorption or reflection of light. When a small current is applied, the particles are aligned, resulting in an increase in the transparency of the glass. LC technology works similarly, with crystals aligning parallel to let light in order to let it pass through when a current is applied. In the absence of a current, the crystals are once again randomly oriented, causing light scattering, and resulting in a translucent appearance. Therefore, this technology is mainly used as privacy glass, as no light is specularly transmitted through it. However, a significant disadvantage of these technologies is the need for the application of a continuous current to maintain the clear state of the glass. In contrast, EC technology works as an optical battery, considering it possesses a so-called "memory effect" that allows it to retain its latest state, whether bleached or colored, even when the current is no longer being applied. Therefore, it is considered superior to SPD and LC technologies in terms of energy efficiency, durability, and convenience.

1.2 Context of the research

During my undergraduate studies in the Engineering physics department at Polytechnique Montréal, I had the opportunity to take a microfabrication course that introduced me to the fascinating world of thin films, micro to nanosized coatings, and their wide-ranging applicability. It was during this course that I first learned about the Functional Coating and Surface Engineering Laboratory (FCSEL) led by Professors Martinu and Klemberg-Sapieha and their close collaborations with industrial partners. One aspect that particularly stood out about the FCSEL was the emphasis on defining projects in partnership with industry, which highlighted the potential for these projects to have a real-world impact. As someone who wasn't quite ready to dive directly into the industry after graduation, I found this situation particularly appealing because it allowed me to gain exposure to academic research and provided a smoother transition towards a career in industry.

Professor Martinu introduced me to the topic of electrochromic materials, and I quickly became interested in their diverse range of applications. What particularly attracted me was the potential for these materials to be used in ophthalmic lenses, which would allow me to easily explain my work to people who may not have a background in science and engineering. The aspect of technology having an immediate visual impact resonated with me and made me even more eager to explore the subject further. In addition, electrochromic materials had been extensively studied at the FCSEL for quite some time now, leading to a recognized expertise in this field.

Indeed, previous students, such as Dr. Bill Baloukas, M.Sc. Hubert Camirand, M.Sc. Julien Gagnon, M.Sc. Francis Blanchard, M.Sc. Louis Dubé-Riopel had all studied tungsten trioxide (WO_3) and nickel oxide (NiO), the two most renowned complementary EC materials, and their application in areas such as security devices, energy-saving applications, and ophthalmic lenses. Louis's work specifically focused on the implementation of these electrochromic materials in an all-solid-state device (ASSD) for ophthalmic applications [8]. However, he encountered short circuit issues that caused self-bleaching of his samples or even a total absence of coloration, which led to difficulties in obtaining repetitive functional ASSDs and a need for their subsequent optimization. Therefore, one of the main objectives of my project was to develop an efficient cleaning and fabrication methodology to avoid these short circuits. By ensuring the proper

functioning of reproducible devices, I would then be able to characterize their performance and optimize them for eyewear purposes.

1.3 Objectives of the project

The **main objective** of this project was to:

Build an all-solid-state device (ASSD) for ophthalmic applications based on electrochromic inorganic materials to control transmission, reflection, and absorption levels.

This project aimed at producing an EC prototype for ophthalmic lenses to obtain a reversible change from a transparent (high transmission) antireflective (low reflection) state to an opaque (low transmission) mirror-like (high reflection) behavior. To achieve this main objective, **four sub-objectives** were defined as follows:

1. Study and optimize the optical properties and electrochromic performance of the constituent EC materials in their bleached and colored states.
2. Define an efficient cleaning protocol and fabrication process to avoid short circuits and ensure the ASSD's proper functioning.
3. Maximize the transmission while minimizing the reflection in the bleached state and *vice-versa* in the colored state. The reflection should exhibit an increase of 10% upon coloration of the EC device from an antireflective (AR) state.
4. Evaluate the long-term durability of the produced EC devices, as well as their environmental and mechanical durability.

The successful completion of this project will lead to the development of a highly efficient ASSD for ophthalmic applications, with potential applications in other fields, such as smart windows or flexible ASSDs for wearable technologies (e.g., textile for displays or camouflage).

1.4 Scientific publication

As indicated above, Sub-objective 3 aims at increasing the reflection of an ASSD upon coloration while being highly transparent in the bleached state, a characteristic which, to the best of my knowledge, has not been investigated in the literature, as most authors usually focus on the

transmission modulation, performance, and durability of their EC devices. Although optical modelling of a standard ASSD architecture does predict a potential slight increase in reflection upon coloration (<1%), experimental measurements on such ASSDs showed a decrease in reflection [8]. To achieve this objective and based on the work of Heo *et al.* [9], we integrated an optical filter based on alternating WO₃ and ITO layers into an ASSD allowing for the creation of a reflection peak at a specific wavelength. This avenue will be thoroughly investigated in Section 5.3, but the first results were very promising and were thus presented at the Optical Interference Coatings Conference (OIC) in 2022 (refer to Table 1-2). The subsequent results pertaining to these structures have been of great interest to Essilor and constitute a future patent application.

Table 1-2: OIC proceeding paper.

M. Crouan, B. Baloukas, O. Zabeida, J. E. Klemberg-Sapieha, and L. Martinu, "WO₃/ITO bilayers for dynamic optical filters," in *Optical Interference Coatings Conference (OIC) 2022*, R. Sargent and A. Sytchkova, eds., Technical Digest Series (Optica Publishing Group, 2022), paper TD.3.

1.5 Outline of the thesis

This thesis is divided into six chapters. In Chapter 1, the subject is introduced, and the reasons for studying electrochromic devices are elaborated. The literature review in Chapter 2 provides an overview of the most important theoretical concepts related to electrochromic materials and ASSDs and summarizes the existing key findings found in the scientific literature. Chapter 3 discusses the methodology used in this study, including the cleaning procedure, the fabrication process, and the characterization techniques for in-depth optical and electrochemical analyses. In Chapter 4, the individual layers used in the final ASSD are characterized, and the different fabrication steps are examined in detail. Chapter 5 evaluates the performance of working ASSDs in terms of transmission and reflection modulation. It also suggests a new ASSD architecture to enhance the reflection modulation based on the concept described in Section 1.4 and evaluates the ASSD long-term durability. This section provides a conclusive answer to whether the research objectives have been achieved. Finally, the thesis concludes with a summary of the main results and

recommendations for future research to improve the performance and functionalities of electrochromic devices for ophthalmic applications.

CHAPTER 2 ELECTROCHROMISM AND ALL-SOLID-STATE DEVICES

2.1 Foreword

This chapter summarizes the various types of EC materials found in the literature. In addition, it focuses on the electrochromic coloration mechanisms, specifically for tungsten oxide (WO_3) and nickel oxide (NiO), respectively, the most common inorganic cathodic and anodic electrochromes. WO_3 has been extensively studied, providing a profound understanding of its coloration and bleaching kinetics. On the other hand, NiO exhibits a more complex structure and chemical response, thus needing further in-depth studies to fully predict its EC dynamics. Following the individual analysis of their EC behavior, this section explains the architecture of an ASSD combining these two materials. The current applications of these EC devices and the associated challenges are then detailed and explained.

2.2 Electrochromic materials

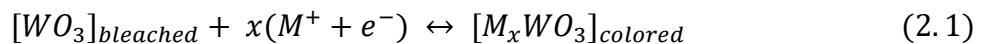
EC materials exhibit a reversible color change through redox reactions involving the insertion and extraction of both ions and electrons when a voltage is applied. These materials can be categorized into two main groups: organic and inorganic. The most common organic ones are organic compounds, or polymers such as viologens, whereas the inorganic materials are mostly transition metal oxides [10]. Organic materials exhibit a larger variety of colors due to their highly flexible composition, as well as faster coloration and bleaching kinetics [11]. Typically, they display transitions between two colors, while inorganic materials vary from a transparent state to a colored state following an increasing absorption of light in the visible spectrum.

Affordable deposition techniques like dip-coating and spin-coating are commonly used for organic compounds, however, their lifetime is often limited due to their sensitivity to UV radiation and oxygenation [12]. This necessitates a more complex design as a result of additional protective layers in EC devices to maximize the material's longevity. Some organic EC materials have already been commercialized, for instance, in the Boeing 787 Dreamliner windows and the Gentex Corporation rear-view mirrors [13]. In contrast, inorganic films require more complex (vacuum-based) deposition systems, such as sputtering or evaporation. These systems provide higher

The most extensively studied cathodic EC material is WO_3 . It displays a transition from a transparent state in the visible region to a deep blue absorbing state with high coloration efficiency and cycling durability. Its electrochromic properties were first discovered in 1815 when Berzelius reported its blue coloration upon hydrogen intercalation [10], but Deb published the first EC device using WO_3 a century later [15]. In this device, two gold electrodes were used, dissociating the water molecules from the ambient air by application of a high voltage. The resulting hydrogen atoms were then intercalated into the WO_3 layer, leading to its coloration. Since then, numerous studies have been conducted to enhance its optical modulation while minimizing the applied potential and its response times. For commercial viability, the device also needs a constant source of ions to ensure stability over time. Hence, more complex architectures were developed using both cathodic and anodic EC materials to work as reversible and controllable EC devices. The most investigated anodic electrochromes are IrO_2 and NiO [10], because of their high coloration modulation and chemical stability. However, considering the recent extensive work performed on NiO at the FCSEL [8], the following work will focus on ASSDs fabricated with WO_3 and NiO , respectively as the cathodic and anodic EC materials. Additionally, NiO displays a complementary brownish color to the dark blue WO_3 color, resulting in an ideal neutral grey color for ophthalmic lenses. The structures and functionality of such ASSD will be depicted in more detail in Section 2.3.

2.2.1 Tungsten oxide

It is necessary to fully understand the electrochromic coloration/bleaching mechanisms in WO_3 to further investigate the performance of EC devices. The following equation describes the simplified reaction leading to the coloration of a WO_3 layer [16].



Here, x is the intercalation ratio, e^- is an electron and M^+ is the ion taking part in the coloration (often H^+ , Li^+ , and Na^+ ions). WO_3 coloration occurs with the simultaneous insertion of ions and electrons for charge balancing. Usually, hydrogen and lithium are preferred because of their small size as ions, which ensures easier diffusion through the EC material. The crystal structure of WO_3 is based on perovskite WO_6 octahedra interconnected by their corners forming triangular and

hexagonal cavities capable of hosting ions [17]. Only H^+ and Li^+ ions are small enough to reach both cavities, while larger ions are limited to the hexagonal spaces. However, a well-ordered crystalline structure increases the film density and prevents the creation of these cavities, hence hindering the diffusion of ions through the layer. Contrarily, polycrystalline (semi-ordered) and amorphous (highly disordered) structures of WO_3 lead to less dense layers, increasing the number of interstitial sites that ions can access. When the coloration voltage is applied in the WO_3 polycrystalline structure, the high concentration of electrons becomes delocalized in the material structure. These free electrons respond to incident light by shielding the internal electronic structure, resulting in high reflection modulations in the near-IR region [10]. However, in this project, the focus is on the amorphous structure of WO_3 , which leads to a significant increase of absorption in the visible spectrum when intercalated, as explained below (any future mentioning of WO_3 will refer to amorphous WO_3).

In its transparent state, WO_3 behaves as a semiconductor; thus, the Fermi level is positioned between its valence and conduction bands. Upon intercalation, the coloration of the material can be attributed to two mechanisms [10]: small polarons absorption due to an excess of electrons creating a localized lattice distortion, and intervalence charge transfer. Essentially, the inserted electrons are localized at the tungsten atoms, resulting in the reduction of W^{6+} to W^{5+} and causing an increase in the Fermi level into the conduction band [18]. This process leads to the photo-induced absorption that occurs with the oxidation of W^{5+} back to W^{6+} . However, during the intercalation of ions, the formation of hydroxyl groups can lead to the generation of W^{5+} and W^{4+} valence sites, resulting in the two other potential charge transfers: $W^{5+} \leftrightarrow W^{4+}$, $W^{6+} \leftrightarrow W^{4+}$. The site-saturation model initially developed by Denesuk *et al.* and further improved by Berggren, describes the probability of having these different intervalence charge transfers as a function of the intercalation level (x) [19, 20].

$$P(W^{5+} \leftrightarrow W^{4+}) = \frac{x^3(2-x)}{8} \quad (2.2)$$

$$P(W^{6+} \leftrightarrow W^{5+}) = \frac{x(2-x)^3}{8} \quad (2.3)$$

$$P(W^{6+} \leftrightarrow W^{4+}) = \frac{x^2(2-x)^2}{16} \quad (2.4)$$

These probabilities are displayed in Figure 2.2, giving the relative number of transitions depending on the ion intercalation levels.

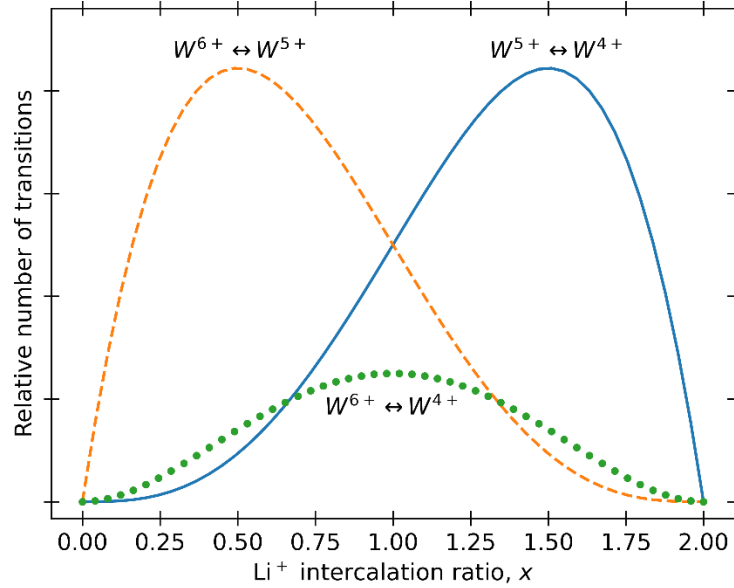


Figure 2.2: Relative number of transitions depending on the intercalation ratio of ions in WO_3 .

The $W^{6+} \leftrightarrow W^{5+}$ transition reaches its maximum value at $x = 0.5$, whereas the $W^{5+} \leftrightarrow W^{4+}$ transition is more likely to occur at much higher x values ($x = 1.5$). The $W^{6+} \leftrightarrow W^{4+}$ transition, however, is less likely to occur but is distributed across the entire range of intercalation ratios considered here. It has been observed that the intercalation ratio should not exceed 0.3-0.4 to ensure a higher level of reversibility of the EC properties of WO_3 [21]. The predominant transition in this range of intercalation ratios is $W^{6+} \leftrightarrow W^{5+}$, which is responsible for the main absorption modulation.

The coloration and bleaching mechanisms of WO_3 have been extensively studied over the years, leading to the establishment of several models to fully understand the charge transfer kinetics. The Cottrell equation is used to evaluate the diffusion of the ions in the device during the coloration of WO_3 by highlighting the expected relationship between the measured current and time [22]:

$$i_c = n_e F A_{WE} C_0 D_i^{1/2} \pi^{-1/2} \frac{1}{t^{1/2}} \quad (2.5)$$

Here, n_e is the number of electrons in the redox reaction (one in the present case), F is the Faraday constant, A_{WE} is the area of the working electrode, C_0 is the concentration of the electrolyte, and D_i is the diffusion coefficient. However, the intercalation of ions in WO_3 is hindered by the potential barrier at the interface with the electrolyte [23] which slows down the coloration process. Conversely, the material can be bleached by applying a reverse potential, leading to the deintercalation of the ions. Faughnan *et al.* [24] demonstrated that the interface with the electrolyte is not a limiting factor in this case. Instead, the ions are mostly constrained by their diffusion through the EC film, and their speed is even assisted by the back electromotive force due to the change in the chemical potential. Consequently, the authors proposed a new definition for the current as a function of time to describe the bleaching process:

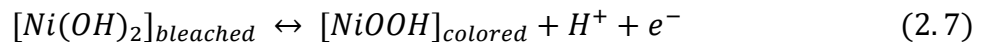
$$i_b = \frac{(p_{H^+}^3 \varepsilon \mu_{H^+})^{1/4} V^{1/2}}{4^{3/4}} \frac{1}{t^{3/4}} \quad (2.6)$$

Here, p_{H^+} is the volume charge density of the protons in the colored WO_3 , ε is the relative dielectric permittivity of WO_3 , μ_{H^+} is the ionic mobility and V is the applied potential. Therefore, the WO_3 bleaching mechanism is expected to be faster than the coloration ($i_b \sim t^{-3/4}$ vs. $i_c \sim t^{-1/2}$).

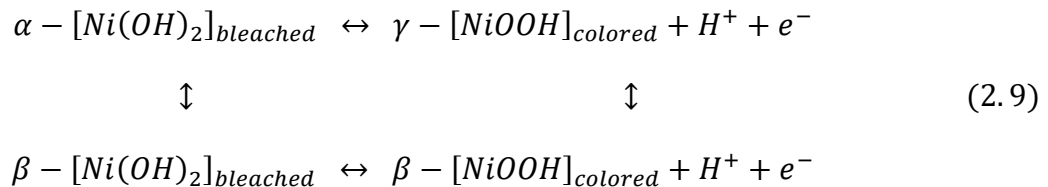
2.2.2 Nickel oxide

NiO has attracted great interest in the scientific community over the years as one of the most studied anodic EC materials. Recent work conducted at the FCSEL was focused on the EC performance of NiO, providing a better understanding of its functionalities and performance [8]. While the coloration and bleaching mechanisms of WO_3 are well understood, there are still some unknowns regarding the EC dynamics in NiO. Using magnetron sputtering, the material can be deposited

either in an Ar + O₂ gas mixture resulting in a brown as-deposited sample, or in an Ar + O₂ + H₂ gas mixture to obtain a transparent material in the form of Ni(OH)₂ [18]. The bleaching of NiO is usually performed in a KOH electrolyte solution, serving as a source of ions for the intercalation phenomenon [25], to produce Ni(OH)₂. However, Avendaño *et al.* [26] established that the oxidation towards nickel oxyhydroxide (Ni²⁺ ↔ Ni³⁺) occurs mainly at the surface of the layer. They demonstrated a decreasing amount of Ni(OH)₂ as a function of depth towards pure NiO. The coloration process generates nickel hydroxide (NiOOH) as ions deintercalate, resulting from the oxidation of Ni(OH)₂. However, there is a divergence in the scientific community regarding the ions contributing to the coloration/bleaching mechanism. Evidence has been found for the presence of both H⁺ and OH⁻ ions [10, 27] in the bleached and colored states, as described by the following equations [16] (note the anodic behavior of the nickel oxide in the equation - compared to the WO₃ - where both the ion and the electron are present in the colored state of the material):



This fundamental distinction in reactions with protons or hydroxyls is one of the main reasons why the EC dynamics in NiO are not yet fully understood. However, Granqvist suggested that the reaction with the proton is more common [10]. This becomes a challenge when trying to model the bleaching and coloration mechanisms of nickel oxide to predict its optical response. The coloration process occurs as a result of the change in the band gap upon the transition from Ni(OH)₂ (p-type semiconductor) to NiOOH (n-type semiconductor), leading to band gap values of 3.6 - 3.9 eV and 1.7 - 1.8, respectively (from absorption spectra) [28]. In addition, both nickel hydroxyl and oxyhydroxide exist in two different forms, as specified by the Bode reaction scheme [29]:



The α-Ni(OH)₂ to β- Ni(OH)₂ phase transition is attributed to the aging of the layer, which corresponds to the dehydration of the material [30]. Specifically, the α phase contains water molecules non-bonded to any atom within the layer, which can be intercalated due to ambient

humidity, or as a result of the redox reaction presented in Eq. (2.8). The phase change induces compressive and tensile stresses in the layer, gradually expelling the H_2O molecules during the application of the cycling potential [10]. This aging phenomenon results in a significant decrease in the interlayer separation, reducing it from 0.7 nm to 0.5 nm [31]. On the other hand, the phase transition from $\beta\text{-NiOOH}$ to $\gamma\text{-NiOOH}$ occurs in the case of overcharging, after a too high charging rate or ion concentration [32].

It is worth noting that $\text{Ni}(\text{OH})_2$ exhibits a slight absorption in the 400-500 nm range, resulting in a yellowish color in its clear state. This characteristic makes it non-ideal for architectural glass or ophthalmic lens applications. However, Avendaño *et al.* [33] explored the addition of Al or Mg during nickel deposition, thus widening the band gap and reducing the absorbance at low visible wavelengths. Although they were able to mitigate this yellow tint, it complicates the deposition process considerably.

2.3 All-solid-state devices

2.3.1 Device architecture

The use of inorganic EC materials has led to the development of ASSDs, typically composed of five layers, excluding the substrate. While glass is a common choice for the substrate due to its high transparency, especially in architectural windows, polymer substrates, such as polyethylene terephthalate (PET), have gained interest for their potential to reduce costs and enable curved or flexible EC devices, particularly in ophthalmic applications. The ASSD architecture involves the cathodic and anodic EC materials separated by an ion conductor and surrounded by two transparent conductive electrodes (TCE):

$$\text{TCE} \mid \text{Cathodic EC material} \mid \text{Ion conductor} \mid \text{Anodic EC material} \mid \text{TCE}$$

It is worth mentioning that all layers are expected to be as transparent as possible in the bleached state of the ASSD. To achieve efficient and durable ASSDs, each layer needs to reach specific requirements, as presented by Granqvist [34]:

- **TCE:** needs to possess a high electronic conductivity to enhance the electron transfer to the ASSD and to ensure a good coloration uniformity of the ASSD (especially in the case of large surfaces), while minimizing its absorption.
- **Cathodic and anodic EC materials:** need to exhibit a significant nano porosity to enhance the insertion and extraction of ions, thus improving their EC performance. They should demonstrate a large coloration and bleaching stability over time.
- **Ion conductor:** needs to possess a very low electronic conductivity with a high ionic diffusion coefficient to allow ions to pass through while blocking electrons.

Two types of ion conductors used in ASSDs are discussed in the literature [35]: “gel-like” polymer electrolytes or inorganic thin films. The use of a gel-like polymer electrolyte offers advantages in terms of easy control over its composition and its strong adherence with the EC materials [10]. However, it complexifies the fabrication process of the devices since the EC materials are most often deposited onto two different substrates and are then laminated with the polymer electrolyte. In addition, despite being a solution to avoid continuous cracks in the device, and thus short circuits, the polymers are more sensitive to UV irradiation and heating. They also need to be sealed to avoid any leakage in the structure. Despite these challenges, products based on the use of a gel ion conductor in architectural windows developed by ChromoGenics are already on the market [36]. On the other hand, while the thickness of the polymer electrolytes is typically in the micron range, solid ion conductors are much thinner (hundreds of nanometers). However, the thinner nature of solid ion conductors can sometimes lead to ASSDs malfunctioning by promoting the continuity of cracks through the device, which may result in short circuits (more details in Section 3.2.1). Finally, one major benefit of the solid inorganic ion conductor is the possibility to use the same deposition system as the rest of the device. Therefore, all the layers can be deposited in a single sequence within the same system. This greatly simplifies the process for industrial production and reduces the number of manipulations of the samples, hence leading to a higher yield of functional ASSDs. Figure 2.3 provides a simplified schematic for the working principle of a standard ASSD.

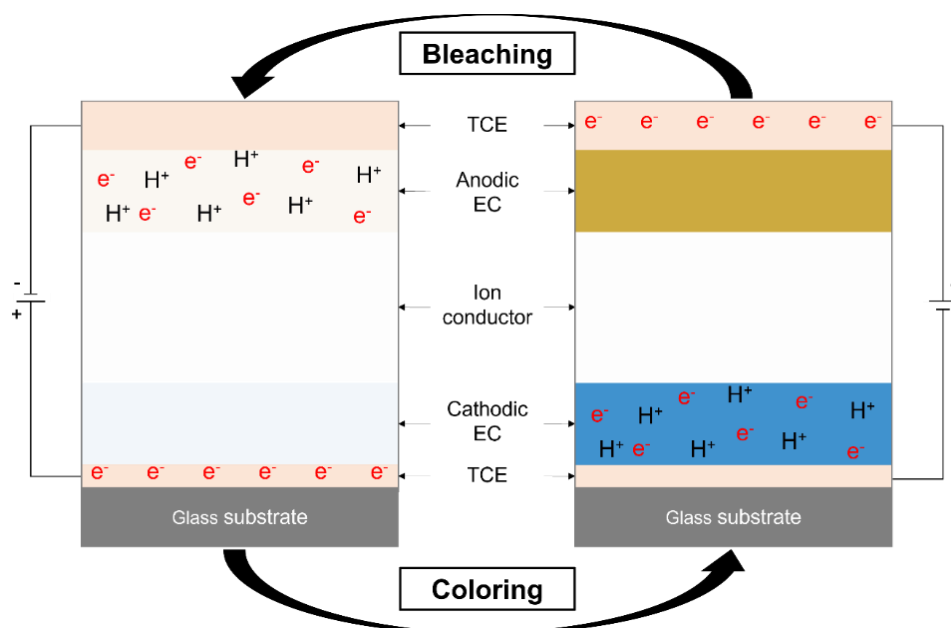


Figure 2.3: Simplified coloration and bleaching processes based on proton diffusion through a standard ASSD.

The H^+ ions can be inserted in the architecture by two methods: chemical pre-intercalation in one of the EC materials immersed in a liquid electrolyte that serves as a source of protons, or physical pre-intercalation by adding H_2 gas in the gas mixture during the deposition of the EC layers.

The coloring process in an ASSD is performed by applying a potential between the two electrodes, creating a displacement of electrons that fill the cathodic electrochrome. The ion conductor, acting as an electronic insulator, blocks the path of electrons, hence provoking an accumulation of electrons at the interface with the cathodic EC material. This results in the migration of H^+ ions through the ion conductor from the ion storage to the counter EC material to achieve charge neutrality. When the applied potential is reversed, protons move back from the cathodic electrochrome through the ion conductor to fill the anodic EC material. As a result, the ASSD can recover its initial bleached state. It also shows the complementary EC behavior of the electrochromes, with the anodic layer coloring upon extraction of the H^+ ions and the cathodic layer coloring when the protons are intercalated. One particular feature of such ASSDs is their memory effect which provides great interest in energy savings. The application of the potential is

only required to initiate a transition between the two states. Figure 2.3 shows how the anodic electrochrome works as an ion reservoir in the bleached state (left) and, accordingly, the cathodic electrochrome in the colored state (right). Additional layers can be integrated into the architecture to provide more functionalities, such as anti-reflective coatings or protective layers. Existing ophthalmic lenses are already composed of thin films providing various features such as scratch resistance and hydrophobicity [37]. Therefore, the incorporation of ASSDs in ophthalmic lenses is expected to be relatively straightforward and advantageous, making them an attractive and practical solution for industrialization.

In the literature, various architectures using different materials have been extensively studied for ASSDs. Table 2-1 provides a few examples of materials that can be used for each layer of the ASSD:

Table 2-1: Examples of materials used in an inorganic ASSD.

Layer	Examples of materials
Cathodic EC material	WO ₃ , V ₂ O ₅
Anodic EC material	NiO, Mg ₄ Ni [38], V ₂ O ₅
TCE	ITO, FTO, AZO [39]
Ion conductor	Ta ₂ O ₅ [40], SiO ₂ [41], ZrO ₂ [42]

The previous sections have presented the reasons for the choice of WO₃ and NiO as the cathodic and anodic electrochromes. The choice of the TCE is crucial to achieve fast and uniform coloration of the ASSD. The most commonly used material is indium tin oxide (ITO) for its excellent combination of high transparency in the visible spectrum and high electronic conductivity. This material has been widely used in electronic devices such as touchscreens or photovoltaics. However, alternative materials have been studied because of the increasing indium scarcity and rising prices [43]. Fluorine-doped tin oxide (FTO) and aluminum-doped zinc oxide (AZO) are two promising alternatives to ITO, as they offer reduced brittleness. However, these transparent

conductive oxides do not reach the same levels of performance in terms of transparency and electrical conductivity as ITO. Another approach is to use metal coatings such as silver (Ag), which possesses the lowest resistivity among metals. However, silver comes with two major drawbacks: it is extremely sensitive to oxidation and leads to higher reflectance and absorption. Hence, researchers are studying the incorporation of a thin Ag layer (~ 15 nm) between two thin dielectric layers (~ 50 nm) [44] as a means of reducing the reflection on the silver surface while protecting the metal from oxidation. Therefore, incorporating designs such as ITO|Ag|ITO [45] or AZO|Ag|AZO [46] offers the advantage of acting as AR coatings while maintaining the high conductivity of the Ag layer. Nevertheless, considering the desire to produce easily fabricated functional ASSDs, the use of thin ITO electrodes remains the most popular approach.

Regarding the ion conductor, Table 2-1 presents various choices that have been successfully implemented in ASSDs. Among these materials, Ta_2O_5 is widely used due to its large band gap, ideal for electronic insulation. Additionally, it presents a negligible level of absorption in the visible and near-IR spectra, rendering it highly transparent.

To characterize the ASSD performance, various metrics have been defined to enable effective comparisons, including [47]:

- **Appearance:** describes the color modification and the uniformity of the coloration over the samples (specifically for large areas).
- **Switching time:** it is the time required to achieve 90% of the transmission or reflection modulation for both the bleaching and coloring phases.
- **Coloration efficiency:** it describes the optical modulation as a function of the inserted charge density. Basically, it characterizes the material's ability to convert the energy from the current into a change in its optical properties. This metric will be defined in further detail, in Section 3.5.5.
- **Cycling durability:** it qualifies the ASSD's lifetime, i.e., the number of cycles during which it maintains its optical modulation without any abrupt loss.

Therefore, an ideal ASSD should provide quick transitions to different levels of coloration to accommodate the user to various light intensities. In addition, it should exhibit great stability over

time to maintain the same bleached and colored states after thousands of cycles. Regarding the application for the eyewear industry, the EC devices should also present a high transmission in their bleached state while maximizing the coloration efficiency.

2.3.2 Applications

Extensive studies were conducted on ASSDs based on the ITO / WO₃ / Ta₂O₅ / NiO / ITO architecture. Early research by Nagai *et al.* [48] demonstrated an impressive performance for such devices, achieving a visible transmission difference of 55.0% upon coloration at 1.5 V. They also observed a small decrease of 4.9% in the visible reflection between the two states of the ASSD. This is very important for this project as Sub-objective 3 relies on obtaining a 10% increase of reflection upon coloration.

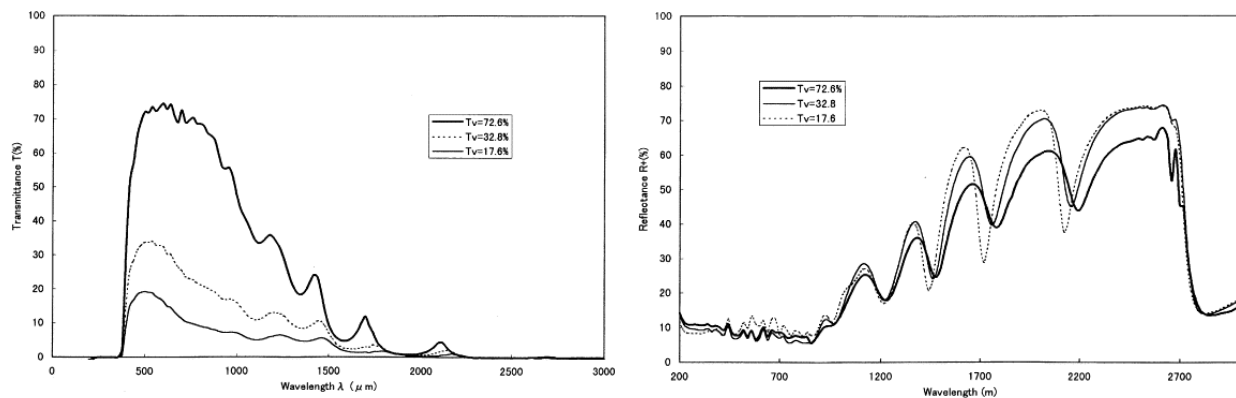


Figure 2.4: Transmission (left) and reflection (right) modulations upon coloration of an ASSD on the solar spectrum. Image taken from [48].

The few studies performed on the reflection modulation do not take into account the transmission modulation of their devices. They aim at obtaining the highest reflection in the bleached state, which results in a lower reflection upon coloration. For instance, Zhou *et al.* [49] obtained a decrease of more than 50% in the colored state. This reduction in reflection is correlated with an increase in absorption, which shows a negative impact on its ability to transmit light. Nonetheless, most studies are directed toward enhancing the transmission modulation and the speed of the coloration mechanisms. For instance, Che *et al.* [50] developed a device exhibiting a large transmission modulation upon coloration. As shown in Figure 2.5, the colored transmission which

is reachable, and the speed of the mechanism are voltage dependent. Indeed, their device showed a ΔT_{550nm} of 11.4%, 21.7%, and 39.3% after 50 seconds of applying 1 V, 2 V, and 3 V, respectively. However, the highest applied potential demonstrated significant degradation, obtaining a colored transmission at 550 nm $\sim 10\%$ higher after 100 cycles, where both the bleached and colored states are impacted. They suggested that a too high voltage may impact the mechanical properties of the materials, hence hindering the passage of both ions and electrons.

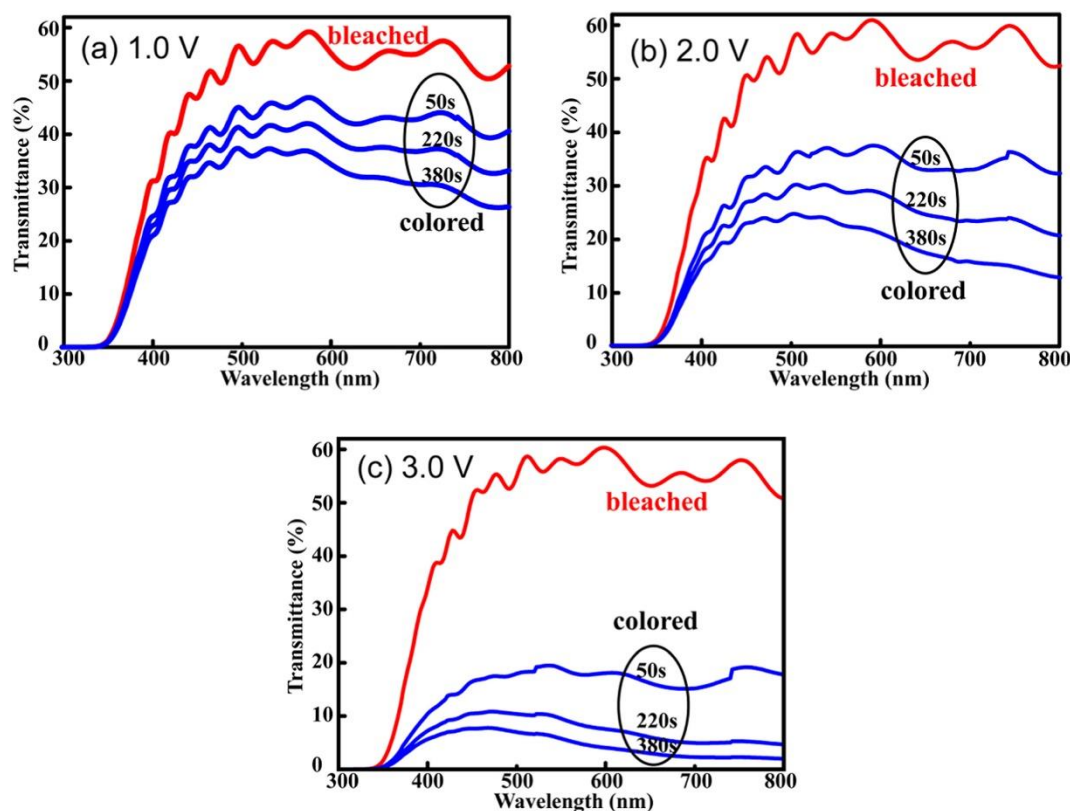


Figure 2.5: Transmission modulation of an ASSD at different voltages. Image taken from [50].

Most of today's research is focused on improving the durability of such ASSDs as they can encounter different issues during extended use. One aspect that is extensively investigated is the choice of ions used for intercalation in the EC materials, which can impact the response time, the optical modulation as well as the reversibility of the device. As mentioned above, the size of the ions plays a critical role in their diffusion through the porous layers of the ASSD. Cui *et al.* has studied the impact of the smallest ions, (H^+ , Li^+ and Na^+) intercalation on the EC performance of

WO₃ [51]. They concluded that Na⁺ ions present high modulation efficiency in the near-IR spectrum. Yet, as it was explained in Section 2.2.1, these ions are not able to reach all interstitial sites in the WO₃ microstructure, hence decreasing drastically its intercalation efficiency. On the other hand, the authors demonstrated that the highest visible modulation efficiency was obtained by Li⁺, while the protons allowed for faster dynamics due to a lower diffusion energy barrier. In addition, the hydrogen ions can bond to the oxygen atoms when intercalated, whereas the lithium ions will be located in the intercalation sites of the crystal. Therefore, the H⁺ intercalation creates a localized lattice distortion, resulting in a higher probability of defect formation in the WO₃. This phenomenon was also reported for NiO [52] when intercalation with hydrogen seemed to accelerate the formation of cracks at the surface of the layer. Consequently, Li⁺ ions showed better stability regarding charge insertion reversibility and transmission modulation.

The use of lithium ions is also often associated with being a potential source of charge trapping in EC materials, hence hindering the EC performance under extended cycling [53]. This results in an inability to completely retrieve their bleached state, leading to a residual, non-desirable absorption in the materials. Typically, this is explained by the fact that the ions reach deep irreversible sites in the EC layer [54]. However, Burdis *et al.* [55] suggested another mechanism, explaining that charge trapping with lithium ions occurs due to their reaction with the excess oxygen atoms trapped in the WO₃ structure during reactive sputtering [56], resulting in the creation of:



They demonstrated that some Li⁺ ions were inserted in the layer but did not participate in the coloration of the WO₃ due to the irreversible reactions with oxygen. The lithium charge trapping phenomenon was also observed in NiO, similar to WO₃ [57]. Vink *et al.* further supported this behavior by establishing a linear relationship between the trapped Li⁺ ions and the excess of oxygen in over-stoichiometric WO₃ [58]. However, recent solutions were presented to successfully allow the de-trapping of Li charges in both WO₃ [59, 60] and NiO [61] through galvanostatic rejuvenation, involving the application of a high voltage over several hours. However, no studies have yet been performed on charge de-trapping specifically in an ASSD. When incorporating hydrogen in EC devices, side reactions may occur due to its interaction with the excess oxygen in metal oxides, leading to the formation of H₂O in their microstructures or the generation of hydrogen

gas from protons and electrons [62]. These side reactions can negatively impact the EC performance by reducing the availability of hydrogen ions for insertion and extraction in the ASSD layers, or by creating bubbles that hinder the device's functionality. On the other hand, higher humidity from the ambient environment appears to enhance the EC performance, resulting in a higher optical contrast ratio and coloration efficiency, while decreasing the response time [63]. Yet, the dependence on environmental humidity may hinder the repeatability of an ASSD's performance, which is not desirable for EC devices in ophthalmic applications. Finally, another significant issue encountered by ASSDs is charge leakage, which can be due to bulk defects in the thin films, thus creating an electrical path between the electrodes through the ion conductor [64]. This can result in short circuits, leading to self-bleaching of the device or even preventing it from functioning [8]. As defined in the introduction, this issue will be addressed in this project to develop a recipe that allows for repetitive functional ASSDs.

CHAPTER 3 METHODOLOGY

3.1 Foreword

This chapter details the systematic approach that was followed to deposit, characterize, and optimize each individual thin film, with the objective of producing functional ASSDs that exhibit a reliable performance. A key aspect of this methodology is the use of a rigorous cleaning procedure to prevent the occurrence of short circuits, which have been a significant problem in previous works performed at the FCSEL [8]. The chapter also provides an overview of the deposition system used to produce the coatings and discusses the importance of selecting appropriate deposition conditions that can affect the optical and EC properties of the materials. Additionally, the chapter outlines the techniques used to characterize the optical properties and EC performance of the films. Finally, it briefly touches upon the use of modelling to aid in the design of optical structures.

3.2 Cleaning methodology

3.2.1 ASSD performance altered by short circuit issues

Proper preparation of the substrates is critical to achieving functional ASSDs. Failure to maintain a clean environment during preparation increases the likelihood of defects and dust on the substrate surface, which can compromise the mechanical properties of the subsequent coatings, as illustrated in Figure 3.1. Defects and particles are typically in the range of tens of nanometers to several microns, and since the coatings used in this project are on the nanometer scale, this can create discontinuities in the films as well as local electric field concentration [65].

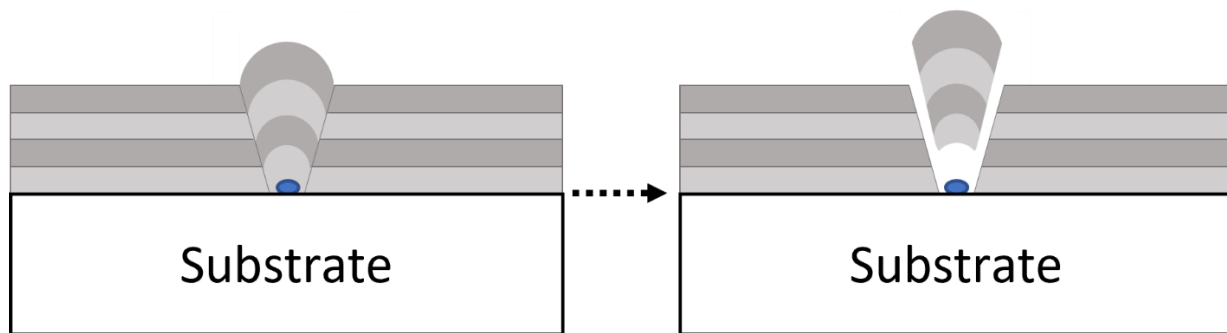


Figure 3.1: Example of cracks (left) and delamination (right) of a coating due to the presence of a defect on the substrate's surface. Adapted from [66].

These defects can create pinholes in the stack, thus breaking the continuity of the thin films, and ultimately impacting the performance of the device. In the case of an EC ASSD, the presence of particles can lead to short circuits and electron paths connected between electrodes, resulting in a rapid self-bleaching of the devices [66]. This issue has been a significant challenge in the past and underscores the importance of ensuring a clean working environment during substrate preparation [67].

Obviously, a direct contact between the bottom and top electrodes can cause an ASSD to malfunction. To prevent any contact, a device can be designed to feature a “terraced” architecture by gradually decreasing the deposition area for each layer, therefore enhancing the device's performance and reliability [68]. Additionally, increasing the thickness of the electrolyte can help address short circuit issues, even though it may result in slower switching dynamics [68]. A buffer layer can also be used to block electrons, reducing current leakage over time [69]. Furthermore, a plasma treatment can be performed on the substrate to remove organic residues and allow surface smoothing [70].

However, the literature is limited on a precise, efficient, and repeatable procedure to eliminate these cleaning issues for EC ASSDs. Therefore, an important part of this work focused on the implementation of a cleaning methodology to avoid short circuits in fabricated ASSDs, which results in more efficient and durable devices.

3.2.2 Substrate preparation before thin-film deposition

A significant amount of time was devoted to developing and testing a robust cleaning methodology for the substrate. For safety reasons, all manipulations involving chemical products should be performed under a laminar flow fume hood to prevent contamination from the ambient air and ensure the safety of the handler. Additionally, it is necessary to wear a laboratory coat and new disposable gloves before handling the samples to avoid contamination. For further protection, it is recommended to use a surgical mask or a face shield to avoid contamination from saliva residue. These measures are crucial to minimize the amount of dust and particles that circulate in the

laboratory environment. It is worth mentioning that the manipulations were not performed in a cleanroom environment, and the fume hood and the deposition system are in different rooms. Consequently, the probability of contamination from the ambient air is significantly increased.

First, to ensure the efficiency of the cleaning procedure, the deionized (DI) water in the ultrasonic bath tank should be renewed before launching the “Degas” function for 5 minutes to remove the air and gas dissolved in the tank. Then, four laboratory beakers containing different solvents are needed: acetone, isopropanol, DI water, and M90 soap diluted in DI water. The three first solvents need to be filled so that the substrates are completely immersed while only a few tens of millilitres of soap are required. Once all of this is prepared, the user should make sure to perform all manipulations while the guillotine of the fume hood is down.

Here is the final methodology which was established for efficient cleaning of the substrates:

1. Immerse the substrate in M90 diluted in water and rub it with the fingers to remove larger particles and dust by mechanical rubbing.
2. Rinse the substrate with DI water before drying using the air knife in the fume hood.
3. Put the substrate in the DI water beaker before inserting it into the ultrasonic bath and start the cleaning procedure for 10 min.
4. Move the sample from the DI water beaker to the acetone beaker and perform another ultrasonic bath cleaning session of 10 min.
5. Move the sample from the acetone beaker to the isopropanol beaker and repeat the ultrasonic bath cleaning process for 10 min.
6. Move the sample from the isopropanol beaker to the DI water beaker and perform a final ultrasonic bath cleaning session of 10 min (this is meant to remove any residue or contaminant from the former solvents).
7. Use isopropanol to clean the substrate holder and the aluminum foil, which is used to protect the substrates during transfer from the fume hood to the deposition system.
8. Install the cleaned substrates on the substrate holder and applied necessary Kapton tape (mask electrode, etc.).

9. Put the aluminum foil on top of the substrate holder.
10. Remove the aluminium foil right before placing the substrate holder in the load lock and launch the pumping procedure on the CMS-18 deposition system.

Finally, once the samples are inserted into the deposition chamber and before depositing the first layer, a plasma treatment can be performed on the substrate surface to remove any residual organic particles and contaminants. This results in the smoothing of the surface, hence improving the adhesion of the subsequent layers. The analysis of the efficiency and reproducibility of this methodology will be shown in Section 4.3.1. The use of the aluminium foil provides an effective protection for the transfer from the fume hood to the deposition system. However, when removing it to insert the substrate holder in the load lock the risk of contamination from the surrounding particles is high. A solution for a future improvement would be to install a laminar flow hood above the load lock to create a particle-free environment.

Before inserting the samples into the deposition system, one can also implement another cleaning step using a CO₂ snow cleaner. Basically, liquid CO₂ is sent through a small nozzle forming CO₂ snow that is ejected at high speed toward the substrate to be cleaned [71]. The particles on the surface are effectively removed through momentum transfer from the CO₂ snow, surpassing the surface bonding forces. In addition, liquid CO₂, which is formed upon a localized increase in pressure during the impact with the surface, shows significant solvent properties for hydrocarbons, resulting in the removal of organic contaminants. However, given that the cleaning procedure was already effective without it, this additional step was judged unnecessary. Also, it was not implemented in the present procedure as the highly pressurized air flow present in this technique often led to the breakage of the thin glass substrates (0.7 mm).

3.3 Thin film deposition

3.3.1 Magnetron sputtering

Considering the variety of applications for thin film technologies, different techniques have been developed to deposit coatings of a specific material under vacuum. The use of a vacuum deposition system is essential to maximize the mean free path of the target atoms, increase the deposition rate,

and limit material loss through collisions with molecules in the ambient air. It also prevents undesired chemical reactions such as oxidation of metals with oxygen or contamination through nitrogen and hydrogen. Several coating fabrication techniques exist that differ in their ability to enhance the deposition rate, stoichiometry, and to control the morphology and structure of vacuum-deposited thin films. The most widely used methods for thin film deposition are chemical vapor deposition (CVD) and physical vapor deposition (PVD) [72]. CVD uses a volatile precursor to chemically react with an inert gas at high temperatures, resulting in the formation of a solid film on the substrate. On the other hand, PVD uses evaporation or sputtering of a solid material, with the ejected atoms from the target material condensing onto the substrate to form a thin film. The PVD process is well suited for large-scale industrial applications due to its ability to produce thin films with enhanced adhesion and low impurity levels. Finally, PVD eliminates the need for hazardous chemicals, making it more environmentally friendly [72]. It also enables depositing materials at low temperatures, making it more suitable for more sensitive substrates such as those used in ophthalmic lenses.

One of the most common PVD methods is magnetron sputtering (MS), which was used in this project. This plasma-based technique allows for the deposition of a wide range of high-purity materials such as metals, ceramics, or alloys using reactive gases and co-sputtering. Furthermore, compared to other PVD methods, it exhibits a high deposition rate combined with good film uniformity, which is crucial for large area substrates [73]. The working principle of non-reactive magnetron sputtering is shown in Figure 3.2.

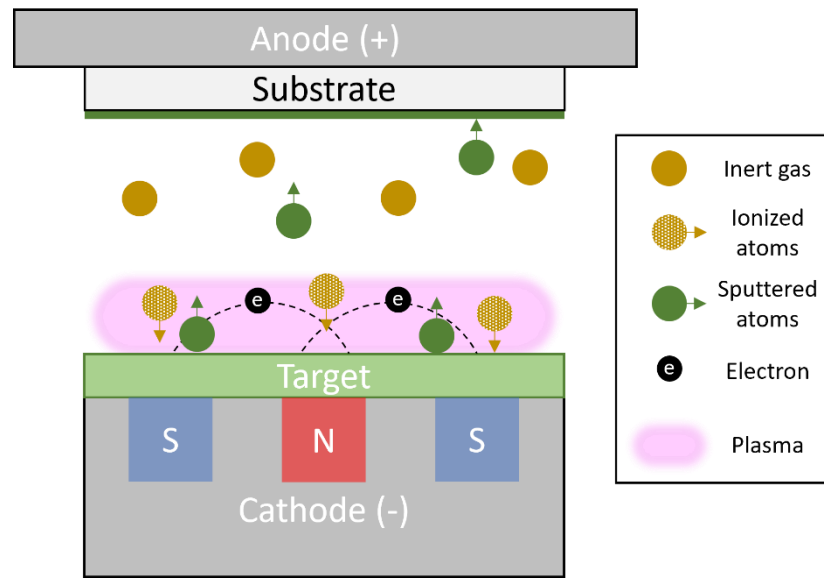


Figure 3.2: Simplified diagram explaining thin film deposition by magnetron sputtering.

A noble gas (e.g.: Ar, Ne, Kr, ...) chosen to prevent any reaction with the target atoms or other gases is introduced in the deposition system. A voltage is applied between the solid target of the material we wish to deposit, and the substrate holder, respectively identified as the cathode (-) and the anode (+). This voltage accelerates free electrons from the gas, causing ionization, and thus, producing more free electrons. It results in the creation of a plasma discharge that is confined near the target due to the magnetic field generated by the magnets placed under the target. As a result, the ions are attracted to the negatively charged target, giving them high kinetic energy to bombard the surface of the material. The impact will create a momentum transfer to the atoms at the surface, which will be dissipated in the material through collision cascades with the atoms and their neighbors in the lattice. However, if the transferred kinetic energy is higher than the binding energy of the atoms in the material, sputtering will occur [73]. These sputtered atoms will be directed toward the substrate facing the target and condense to form a thin film. Additionally, the ion bombardment of the target leads to the release of secondary electrons from the target material. These electrons are trapped in the plasma and actively participate to the ionization; hence contributing to the sustainability of the plasma discharge [74]. A final critical aspect of magnetron sputtering is the requirement for high vacuum conditions to optimize the mean free path of ionized and sputtered atoms which is inversely proportional to the working gas pressure. Indeed, higher pressures result in a higher concentration of gas, leading to more collisions between particles in the

deposition chamber, thus reducing the mean free path of the neutral atoms, ions, and sputtered atoms. In addition, the sputtered atoms collide with a higher concentration of neutral gas, which increases scattering. Therefore, the energy flux of the sputtered atoms reaching the substrate surface is decreased leading to less uniform and more porous film [75].

3.3.2 Deposition system

In this project, thin film deposition by magnetron sputtering was performed using a CMS-18 system by Kurt J. Lesker (see Figure 3.3).

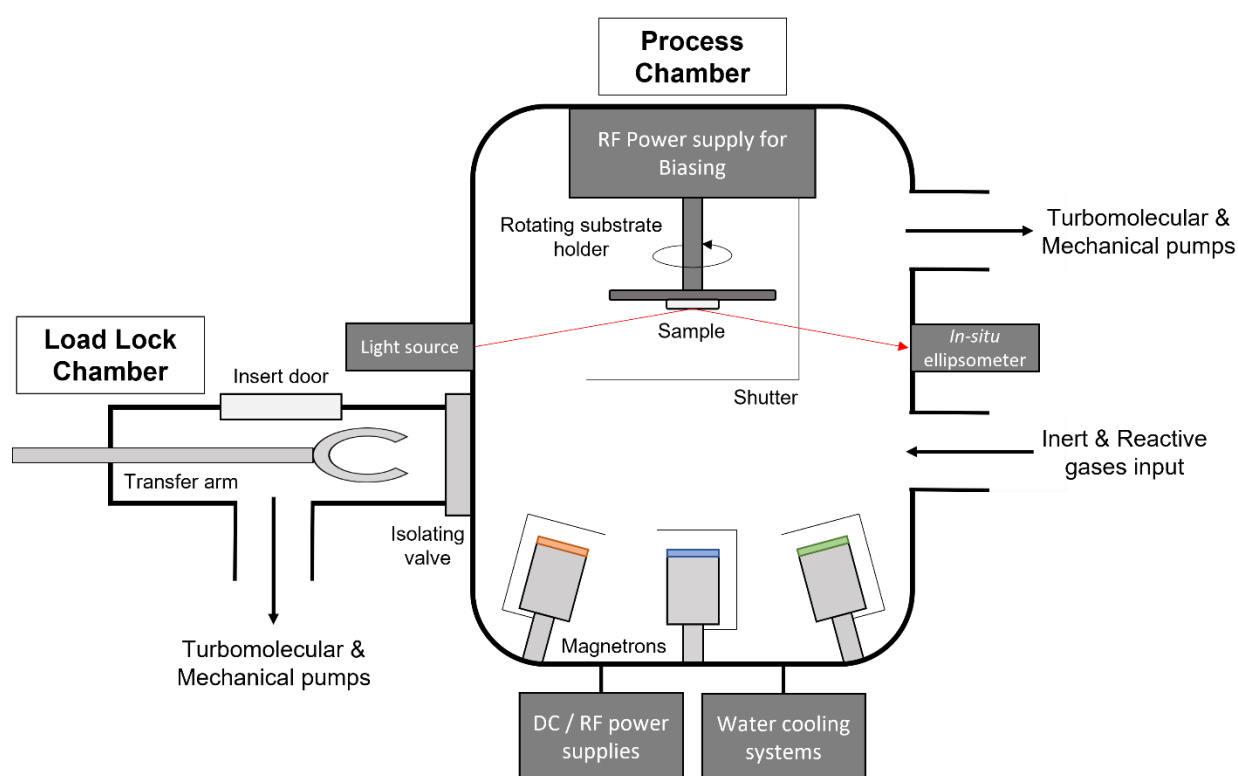


Figure 3.3: Schematic representation of the CMS-18 system used for magnetron sputter deposition.

The CMS-18 possesses two chambers: a load lock chamber and a process chamber. To keep the system under vacuum, the chambers are connected to separate pumping systems composed of turbomolecular pumps connected to a common mechanical backing pump that keeps the base pressure of the process chamber at $\sim 9 \cdot 10^{-8}$ Torr. A gate valve separates the two chambers allowing

the samples to be inserted and extracted in the load lock chamber at atmospheric pressure without breaking the vacuum of the process chamber. When the load lock chamber reaches $5 \cdot 10^{-5}$ Torr, the substrate holder is transferred into the process chamber on a rotative stage. Prior to depositing the films, the water cooling must be checked to ensure the integrity of the magnetrons which can be damaged by the heat generated during deposition. Indeed, the magnets could be demagnetized if the temperature on the magnetron exceeds the Curie temperature of the magnet material, leading to the instability of the plasma discharge [76]. The system allows up to four 3-inch magnetrons and a 2-inch center magnetron to be installed in the process chamber, allowing different materials to be deposited sequentially or simultaneously (e.g.: co-sputtering). To prevent deposition during the target conditioning phase, each magnetron is equipped with a shutter that can be remotely opened and closed. The magnetrons can each be run in either direct current (DC) or radiofrequency (RF) mode depending on the type of material target which is used. The DC power supply was used in this project to apply power to the metallic targets: W, Ni (93%)-V (7%), and Ta while RF magnetron sputtering was employed for non-conductive ceramic targets such as SiO_2 . It was also used for the ITO (90:10%wt), as the conductivity of the coatings were better in RF than in DC sputtering (more details will be given in Section 4.2.1). The system also allows the introduction of reactive gases (O_2 , H_2 , N_2) to control the gaseous environment during the deposition. This allows one to broaden the range of materials that can be used as thin films by depositing oxides and nitrides from elemental material targets with specific composition. Finally, an M-2000 *in-situ* ellipsometer from J.A. Woollam Co. is also installed on the system to enable *in situ* monitoring and assessment of the thickness and optical properties of the deposited layers.

The CMS-18 is fully automated and allows for the control of multiple parameters including gas pressure, applied power to the target, and reactive gas flows. The choice of deposition conditions has a direct impact on the energy flux of the sputtered atoms, which affects the deposition rate, density, stoichiometry, and crystallinity of the deposited thin films. For instance, as explained in the previous section, a higher working pressure reduces the mean free path of the sputtered atoms as a result of multiple collisions, decreasing the density of the film. On the other hand, a higher discharge power increases the kinetic energy of ions in the plasma, leading to a more energetic ion bombardment on the target surface [77]. Thus, this results in more energetic flux of atoms reaching the substrate, producing denser films with higher deposition rates [78].

The fabrication of ASSDs in this project involved depositing metal oxides (WO_3 , Ta_2O_5 , NiO) from pure metal targets, and the desired stoichiometry of the deposited material can be achieved by controlling the flow of reactive gases [79]. The reactive gas is used to provoke chemical reactions between the sputtered metal atoms and the reactive gas, resulting in the formation of compounds on the target and on the substrate surfaces. For all the metallic targets, a hysteresis curve of the target voltage vs oxygen content was drawn to determine the range of O_2 vs Ar concentration suitable for optimal deposition conditions. Figure 3.4 illustrates the hysteresis curve obtained for the Ta target.

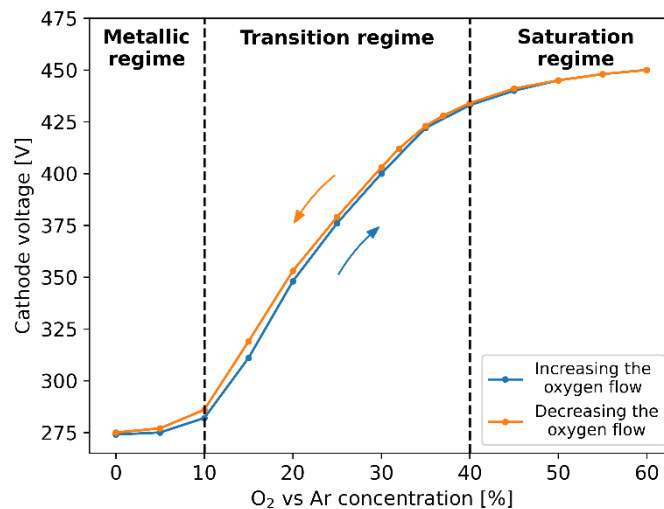


Figure 3.4: Example of the hysteresis curve obtained for the Ta target.

The hysteresis can be divided into three distinct regions: the metallic, the transition, and the saturation regimes [80]. At low oxygen concentration, the deposited film exhibits a metallic or sub-stoichiometric behavior because of an insufficient concentration in oxygen in the gas. By increasing the oxygen content, the metallic target undergoes a transition regime, reacting with the reactive gas to form a metal oxide on its surface. This results in an increase in the cathode voltage and the sputtering rate. Eventually, at a critical level of oxygen content, the cathode voltage enters the saturation regime, where the rate of oxide formation on the surface reaches the sputtering rate. If it exceeds the sputtering rate, the target enters a poisoning regime, which causes a decrease in the deposition rate over time, impacting the linearity of the deposition conditions [81]. The optimal

oxygen concentration can finally be chosen from the hysteresis curve in the transition regime, near the saturation region, to efficiently form the desired compounds while maintaining a desirable deposition rate. It is worth noting in Figure 3.4 that the cathode voltage does not return to the same values when the oxygen flow is decreased, until it recovers its initial value. This hysteresis effect highlights the dependence of the deposition process with respect to the target's operating history.

To ensure reproducibility under the deposition conditions of the desired compound, the targets were always pre-sputtered in pure Ar for 10 minutes prior to any deposition. This enables one to remove any compound formed on the target surface, allowing the deposition to start with a target of pure elemental material. Additionally, other factors such as the substrate distance from the target and deposition temperature can also influence the properties of the deposited coatings; in the present case, the distance was fixed at 25 cm and all films were deposited at room temperature. Table 3-1 summarizes the optimal deposition conditions used for the fabrication of the ASSDs. Details explaining the choice of these conditions will be given in Section 4.2.1.

Table 3-1: Deposition conditions for all the materials incorporated in the EC ASSD.

Material	Type of MS	Power density (W/cm ²)	Pressure (mTorr)	Gas proportion (%)			Deposition rate (nm/min)
				O ₂	H ₂	Ar	
WO ₃	DC	5.48	10	35	0	65	16.4
Ta ₂ O ₅	DC	9.87	7.5	55	0	45	15.1
NiO	DC	5.48	10	6	25	69	12.0
ITO	RF	2.19	1	0	0	100	2.1

3.3.3 Control over the thin film's microstructure

Considering the numerous parameters that can influence the properties of the thin films, Anders extended the structure zone diagram (SZD) as shown in Figure 3.5 [82].

This diagram highlights the significant impact of both substrate temperature and kinetic energy of the ions on the microstructure of thin films during growth. It shows that at low E^* thin films tend

to be thicker, more porous, and amorphous, which is ideal for EC materials in an ASSD as discussed in the previous chapter (see Section 2.2.1). However, when the kinetic energy of the bombarding particles is higher, the resulting coatings become denser and more crystalline. In this case, resputtering is also possible, as highly energetic ions can cause the ejection or sputtering of atoms from the film surface, which are sometimes redeposited onto the sample [83].

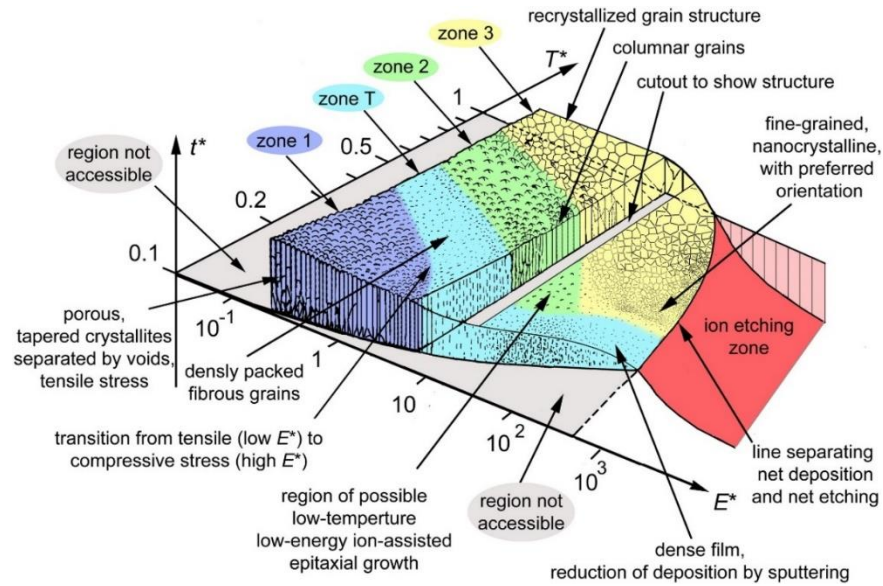


Figure 3.5: Anders's SZD, where t^* represents the net film thickness, T^* the generalized substrate temperature, and E^* the normalized energy of the ion flux, which describes the kinetic energy of the bombarding particles on the substrate. Image taken from [82].

The diagram's far right section shows the ion etching zone, where the ion kinetic energy E^* is very high. In the deposition system shown in Figure 3.3, an RF power supply is connected to the rotating substrate holder, allowing for the generation of a plasma contained near the substrate, where the high negative potential (bias) attracts ions from the inert and reactive gases toward the sample. Biasing during deposition enhances the kinetic energy of bombarding particles on the surface, allowing for the densification of the film as previously explained. In addition, bias-induced ion bombardment can be used for two purposes: pre-cleaning of the substrates and treating the film surface. The latter can result in reducing the roughness of a layer and, therefore, favor a better adhesion for subsequent coatings [84]. This was implemented in the current project to favor growth

dynamics, as the top ITO layer's conductivity was shown to be highly dependent on the smoothness of the underlying film. This will be explained in Section 4.3.2, along with a detailed description of the device fabrication step sequence.

3.4 Optical characterization

3.4.1 Spectrophotometry

Spectrophotometry is used to measure the reflection (R), transmission (T), scattering (S) and thus calculate the absorption (A) knowing that: $A + R + T + S = 1$. In this project, the properties of each material, as well as the EC materials in their bleached and colored states, were measured using a Cary 7000 spectrophotometer equipped with a universal measurement accessory (UMA) from Agilent Technologies. It enables the measurement of R and T from 250 nm to 2500 nm at different angles (from 6° to 85°).

For eyewear purposes, it is important to use a method for comparing the efficiency and properties of different samples. The International Commission on Illumination (CIE) developed, in 1931, a color space that enables the representation of colors according to human perception. By using reflection or transmission spectra, it provides the calculation of the color of an object under various light source illumination. In this project, calculations were performed using the CIE D65 standard illuminant and the CIE 1931 2° observer color matching functions. One important metric used for comparison is the luminous reflectance or transmittance, denoted as Y_{lum} (Y being R or T), which quantifies the percentage of visible light that is reflected from the surface of an object or transmitted through it:

$$Y_{lum} = \frac{\int_{Vis} Y_{meas} \bar{y} I d\lambda}{\int_{Vis} \bar{y} I d\lambda} \quad (3.1)$$

where Y_{meas} is the data from the measured sample, $\bar{y}$ corresponds to the photopic luminous efficiency curve, and I is the illuminant. In the context of eyewear, acquiring the luminous reflectance or transmittance is essential because it provides a more faithful representation of what the end user perceives.

3.4.2 Spectroscopic ellipsometry

Spectroscopic ellipsometry is often used for its simplicity and the amount of information it can provide. Light is generated by a light source which is sent through a polarizer and a rotating compensator, which results in a known polarization. The beam is then reflected on the sample, modifying the phase and amplitude of the polarization. Afterwards, the light goes through another rotating compensator and polarizer. Finally, the reflected light is collected by a CCD detector, which allows for fast and accurate measurements. The change in polarization is defined by the following:

$$\rho = \frac{-r_p}{r_s} = \tan(\Psi)e^{i\Delta} \quad (3.2)$$

representing the complex ratio of the Fresnel reflection coefficients in p and s polarization; and where Ψ and Δ represent the amplitude ratio and phase delay between the polarizations respectively.

The present ellipsometric measurements were performed with a RC2-XI spectroscopic ellipsometer from J.A. Woollam Co. which allows for a wide wavelength range (from 210 nm to 2500 nm) and measurements at multiple angles, usually 45°, 55°, 65°, and 75°, for 10 seconds each. Once the data is acquired as a function of wavelength and incidence angle, it can be analyzed through the *CompleteEase* software, also from J.A. Woollam Co. For a single layer, general oscillator models are used to model the layer's optical properties in which oscillators can be added to simulate different physical phenomena within the material, the main ones used in this project being:

- Tauc-Lorentz: simulates the band gap behavior of the studied material.
- Gaussian: simulates the absorption bands of the studied material.
- Drude: simulates the dispersive behavior of metals due to the presence of free electrons.

Finally, after fitting the model, we obtain information on surface roughness, thickness (d), optical properties (refractive index, n , and extinction coefficient, k), and anisotropy. The fit quality of the model is given by a mean square error (MSE) calculated by the software. To ensure that the optimization algorithm converges to the desired solution, the user must supply initial approximate

values for the physical properties and thickness. Otherwise, the algorithm can get stuck in a local minimum and fail to identify the absolute minimum. Therefore, if the initial parameters are too far from the actual values, the fitting of the model can give a low MSE with non-realistic values. It is also possible to import R and T measurements obtained from spectrophotometry to enhance the accuracy of the model.

3.5 Electrochemistry

3.5.1 Cyclic voltammetry and *in-situ* transmission measurements

The electrochromic properties of the samples were characterized by cyclic voltammetry, which measures the induced current following the application of a known potential. The electrochemical charge insertion (H^+ ions) is performed by a three-electrode setup, where the reference electrode (RE) is a saturated calomel electrode (SCE), and the counter electrode (CE) is a platinum electrode. The latter has been chosen because of its noble metal characteristics and resistance to oxidation. The third and final electrode is the working electrode (WE) which, in the present case, is the sample under analysis. The three electrodes are immersed in a cell filled with an electrolyte solution serving as the source of ions for intercalation tests. When analyzing the WO_3 samples, an acid solution of 0.1 mol/L of H_2SO_4 was prepared. However, the NiO EC properties were measured in a 1 mol/L of KOH solution since the acid solution was too aggressive and led to complete delamination of the coating. The three electrodes are then connected to an Autolab PGSTAT204 potentiostat from Metrohm which enables the application of a given potential measured between the RE and WE while measuring the resulting current between the WE and CE. All measurements were controlled by the *Nova* software which allows customized recipes for electrochemical charge insertion.

The electrochemical cell is installed on an optical table enabling *in situ* transmission measurements to study the evolution of the transmission from the bleached state to the colored state of the sample, as schematized in Figure 3.6. This setup consists of a halogen lamp, which sends light through several optical lenses, enabling to focus the light on the sample of interest. The transmitted light through the sample is then projected onto an optical fiber, connected to a *MultiSpec Pro* module

from Tec5 which displays and saves the transmission in real time in a wavelength range of 400 nm to 900 nm.

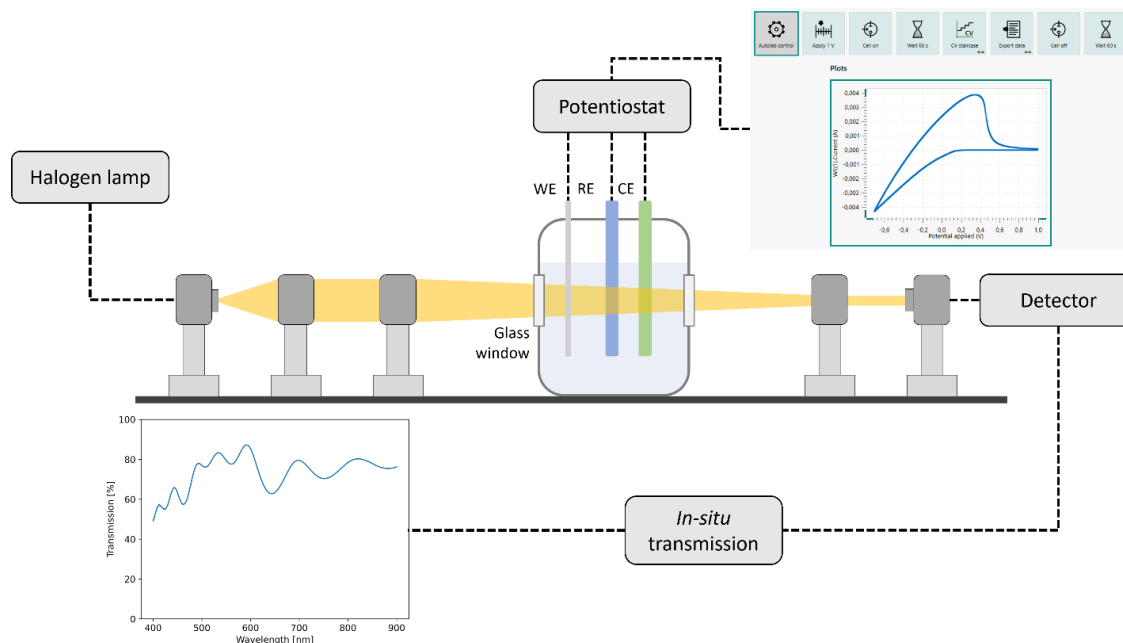


Figure 3.6: Setup used for the electrochemical and the *in situ* transmission measurements.

3.5.2 Cyclic voltammetry recipe

Cyclic voltammetry (CV) is used to study the EC properties of a material. The experiment relies on applying a linear voltage sweep between two specified potential values at a constant scan rate, in both forward and reverse directions. The resulting current response is collected, and the experiment can be repeated for multiple cycles, providing valuable information about the time evolution of the material's EC performance. For instance, it allows one to determine the number of cycles needed to fully activate the EC behavior of a material, but also characterize its stability over time, illustrating the potential degradation of the EC properties.

Figure 3.7 shows typical cyclic voltammograms for (a) WO_3 and (b) NiO layers with their corresponding complementary EC behavior: the red part relates to the bleaching phase of the sample while the purple rectangle represents the coloring phase of the sample. The following recipes enabled the characterization of the EC properties of our films. For the WO_3 layer (NiO

layer) a constant potential of +1 V (-0.6 V) is applied for 60 seconds to fully bleach the material. Then, the potential is linearly varied for 30 cycles from +1.0 V to -0.7 V (from -0.6 V to 0.6 V) and *vice-versa* at a scan rate of 25 mV/s for both materials.

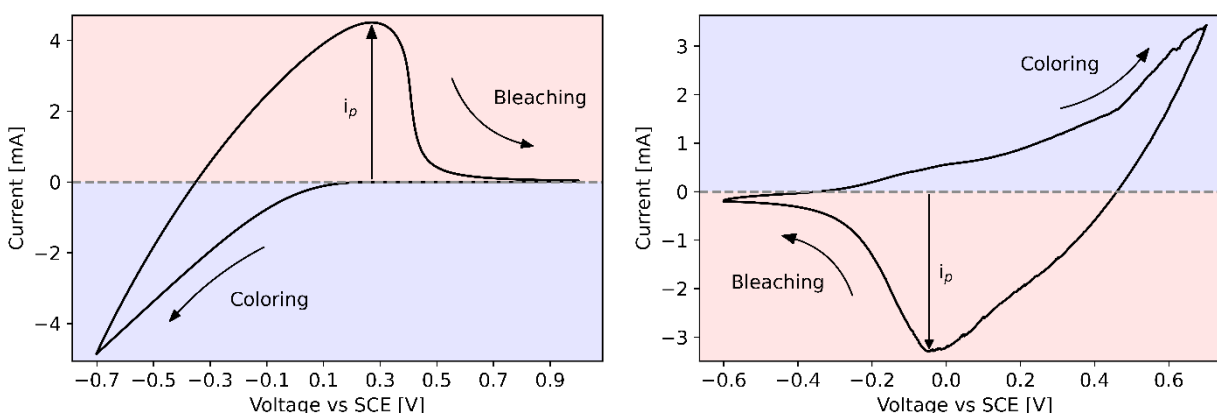


Figure 3.7: Cyclic voltammograms of (left) a WO_3 layer in a 0.1 mol/L of H_2SO_4 solution, and (right) a NiO layer in a 1 mol/L of KOH solution.

3.5.3 *In situ* transmission measurements

The optical characterization of the coloration and bleaching of the samples during CV can be measured using the *in situ* transmission setup presented in Figure 3.6. The methodology for such measurements starts with letting the halogen lamp warm up for 30 minutes to ensure the stability of the light source. Then, the cell is filled with the required electrolyte solution. A reference measurement is performed prior to installing the sample. Then, the platinum and saturated calomel electrodes are installed in the cell and connected to the potentiostat. The sample is mounted in the setup and connected to the potentiostat, with the coating facing the electrodes. Prior to the measurements, the parameters from the *MultiSpec* software need to be adjusted: in this project, 2 measurements/second are saved to ensure the best visualization of the transmission evolution over time.

3.5.4 Chronoamperometry and *in situ* measurements for the ASSDs

The methodology employed for characterizing and analyzing the performance of ASSDs differs from the CVs shown previously. The *in-situ* transmission measurement set-up is slightly changed by replacing the cell containing the liquid electrolyte with a sample holder that does not impede the passage of the light beam through the sample. In this case, the RE and CE are both connected to the bottom electrode of the ASSD, while the WE is connected to the top electrode. For this project, chronoamperometry was used to measure the current evolution as a function of time by applying alternating potentials of +3 V and -3 V for one minute each. These potentials are used to respectively bleach and color the device for a specified number of cycles. The selection of these potentials is crucial to avoid premature device degradation, as choosing too high values can lead to irreversibility in the coloration/bleaching processes [85]. To complete the characterization of the ASSD's optical properties, a new set-up for *in situ* reflection measurements was devised as shown in Figure 3.8. Essentially, the core of the optical fiber sends light onto the sample, and the reflected light is collected by six receptors in the cladding of this same fiber.

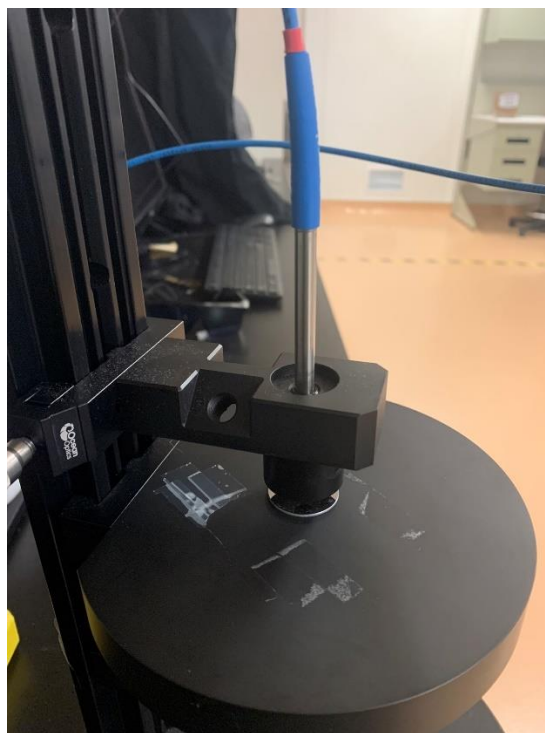


Figure 3.8: Picture of the set-up for *in-situ* reflection measurements.

The reference was established using a 1 mm thick Si wafer, known to be highly specular, prior to the measurements of the ASSD. The reflection of the reference wafer over the visible spectrum was previously measured using the UMA to establish the baseline for 100% reflection during the *in situ* measurements. Hence, to retrieve the actual reflection values of the ASSD, a simple cross-product calculation was performed. Several tests were conducted to ensure the reliability and validate the accuracy of the retrieved *in-situ* spectra, with the relative error not exceeding 2%.

3.5.5 Analysis of the EC performance

Based on the cyclic voltammograms, the EC performance of the layers can be quantified. The Randles-Sevcik equation gives the relation between the maximum anodic current (i_p), which can be read directly from the data as shown in the Figure 3.7, and the diffusion coefficient of ions (D_i) of the studied materials:

$$D_i = \frac{R_g T_a}{n_e F v} \left(\frac{i_p}{0.4463 n_e F A_{WE} C_s} \right)^2 \quad (3.3)$$

Here n_e is the number of electrons that participate in the redox reaction, F is the Faraday constant, A_{WE} is the working electrode area immersed in the electrolyte, C_s is the solution concentration, v is the scan rate used during the cyclic voltammetry, R_g is the universal gas constant, and T_a is the ambient temperature.

The increment of time (Δt) can be determined with the increment of potential and the scan rate used during the CV. This enables the summation of the negative current by this Δt to obtain the total of inserted charges into the coating, while multiplying with the positive current will give the total of extracted charges. This can be useful when it comes to characterizing the long-term durability of the coating as the ratio of inserted versus extracted charges gives an indication about charge trapping in the material or the presence of secondary reactions which could be the result of non-reversible processes.

Another important variable that can be calculated from the results of the cyclic voltammetry is the intercalation ratio x :

$$x = \frac{Q_i M}{e A_{WE} d \rho_M N_A} \quad (3.4)$$

where Q_i is the number of inserted charges, e is the elementary charge, N_A is the Avogadro constant, A_{WE} is the working electrode area, and d , M , and ρ_M are respectively the thickness, the molar mass, and the density of the studied film. The advantage of the intercalation ratio is its consideration of the properties of the coating, which, when comparing two different samples of the same material, gives a better and more precise comparison of the EC properties.

The density ρ_M of the studied thin film can be calculated through the packing density (P) based on the Lorenz-Lorentz effective medium approximation (EMA):

$$\rho_M = P \rho_b = \frac{(n_f^2 - 1)(n_b^2 + 2)}{(n_f^2 + 2)(n_b^2 - 1)} \rho_b \quad (3.5)$$

where ρ_b is the material's bulk density, and n_f and n_b are, respectively, the refractive indices of the chosen material in thin film form, as determined by ellipsometry, and bulk form (2.5 for WO_3 [86] and 2.18 for NiO [87], all at 550 nm).

As shown in the setup (see Figure 3.6), the *in situ* transmission can be measured while performing the CV. This enables us to obtain the EC properties and the associated transmission evolution in real time. Thus, the calculation of another important criterion for EC materials, called the coloration efficiency η , can be carried out:

$$\eta = \frac{\Delta OD}{Q_i} = \frac{\ln\left(\frac{T_b}{T_c}\right)}{\frac{Q_i}{A_{WE}}} \quad (3.6)$$

where ΔOD is the change in optical density, Q_i is the number of inserted charges, T_b and T_c are, respectively, the transmission in the bleached and colored states, and A_{WE} is the working electrode area.

Finally, another characteristic that is of interest is the response time (τ) of the sample. To help compare with the literature and from one sample to another, it is common to calculate the time taken by an ASSD to reach 90% of its maximum transmission modulation between the colored and bleached states.

3.6 Optical designs

Prior to the fabrication of an ASSD, modelling plays an important role in predicting its optical performance. Two software were used during this project, the first one being *OpenFilters*, an opensource software developed by the FCSEL. Using the optical properties (n and k) of the materials obtained by ellipsometry, the software can calculate the transmission, reflection, color, and other optical properties of a single layer, stacks, or graded-index filters by employing the matrix approach [88]. It also offers the possibility to add target properties for optimization purposes, which is particularly valuable when designing complex optical filters. For instance, when modeling an antireflective ASSD by adding a SiO_2 layer on top of the device, the optimization algorithm can be directed to reach a minimum R_{lum} . As a result, the algorithm will fine-tune the thickness of the layers to achieve the desired optical performance.

The other modelling software was *Essential Macleod*. Although its interface is less user-friendly than *OpenFilters*, *Essential Macleod* has the advantage of being able to implement what are termed “Agile Materials”, i.e., materials that undergo changes in their optical constants due to an external stimulus, such as EC materials. By adding the optical constants of the material in different states, it is possible to specify transmission and reflection targets for both the bleached and colored states simultaneously. Therefore, it was particularly useful in meeting Sub-objective #3 (see Section 1.3) as it was possible to fit the thicknesses of the ASSD layers which would allow to achieve a minimum reflection in the bleached state while also displaying the highest possible reflection in the colored state.

To thoroughly investigate the effects of varying the thickness of the ASSD layers on the transmission and, particularly, the reflection modulation, a custom Python script was developed at the FCSEL [8] and employed. The script adopts the matrix approach to determine R_{lum} and T_{lum} in the bleached (B) and colored (C) states of the ASSD. The thicknesses were varied at 5 nm intervals within the following ranges, and further refined at 1 nm in a more restricted range of values (10 nm interval) once a solution was found:

- SiO_2 & top ITO: from 50 to 150 nm.

- Bottom ITO: fixed at 30 nm (commercial ITO-coated glass substrate from Delta Technologies).
- NiO & WO₃: from 200 to 500 nm.
- Ta₂O₅: from 500 to 800 nm.

Using a brute force approach based on finding the best solution within all modeled architectures, the optimal thicknesses of the different layers in the ASSD allowing to reach the lowest bleached reflection (R_{lum_B}) or the highest possible modulation of the reflection upon coloration ($\Delta R_{lum} = R_{lum_C} - R_{lum_B}$) can be determined. However, to fulfill Sub-objective #3, these two possibilities were combined in a single figure of merit: $\Delta R_{lum}/(R_{lum_B})^3$ (more weight was added to the bleached state reflection R_{lum_B} to prioritize the AR behavior). The optimal architectures were then reproduced in *Essential Macleod* to model the optical response in terms of reflection, transmission, and absorption.

CHAPTER 4 UNDERSTANDING AND OPTIMIZING THE FABRICATION OF ASSDS

4.1 Foreword

Following the description of the methodology employed in this project, this chapter presents the efforts made to ensure the successful fabrication of functional EC ASSDs. The initial step involved the characterization of each layer of the ASSD to analyze their optical properties and EC performance. Additionally, various coloration states of the EC materials were studied to enable accurate modeling and prediction of the response of the ASSDs. Furthermore, a reliable and effective cleaning procedure and fabrication methodology were developed and validated to ensure the functionality of the fabricated ASSDs.

4.2 Layer optimization

4.2.1 Deposition conditions for enhanced optical and EC properties

Prior to focusing on the ASSD, it is crucial to enhance the optical properties and EC performance of each layer. Each material was deposited under different working pressures, and the O₂, H₂ and Ar concentrations in the gas mixture were varied. All depositions were performed while rotating the substrate holder at 15 rpm to ensure higher uniformity of the films. The objective was to find a good balance between enhancing the porosity of the films to promote ion diffusion and maintaining sufficient transparency in the bleached state and optimal EC properties. The final choice of deposition conditions for each thin film is based on a trade-off between the highest modulation of transmission during coloration (ΔT_{550nm}) and coloration efficiency (η_{550nm}).

Optimization of the WO₃ layer's EC properties

The first studied layer is the EC WO₃ material. Park *et al.* [89] showed that DC magnetron sputtering (DC-MS) provides the highest deposition rate, making it ideal for industrial applications, and the fastest bleaching and coloration processes along with a high transmittance modulation. Atak *et al.* [90] also showed that the applied power density to the magnetron influences the performance of the coating, as excessively energetic ionized atoms will lead to a denser film, hence badly impacting the overall performance. Thus, the power density used here is based on previous

FCSEL work [8], while the impact of pressure and reactive gas concentration was studied by CV combined with *in situ* transmission (see Figure 4.1). Initially, the pressure was varied for different samples with an arbitrary value of 30% O₂ vs Ar concentration. The best EC performance was achieved at 11.8 mTorr, which was the highest working pressure achievable by the system with the chosen reactive gas concentration. Therefore, to extend the oxygen range that can be reached, a working pressure of 10 mTorr was chosen to derive the hysteresis curve of the target voltage vs oxygen content to determine the range of O₂ vs Ar concentration suitable for optimal deposition conditions. It was found that a concentration of 20% O₂ vs Ar led to a sub-stoichiometric film due to the metallic state of the target, whereas concentrations of 40% and higher showed a significant decrease in the deposition rate due to target poisoning. The oxygen concentration thus varied between 22% and 35%. Each thin film was deposited at room temperature with a power density of 5.48 W/cm² for 20 minutes.

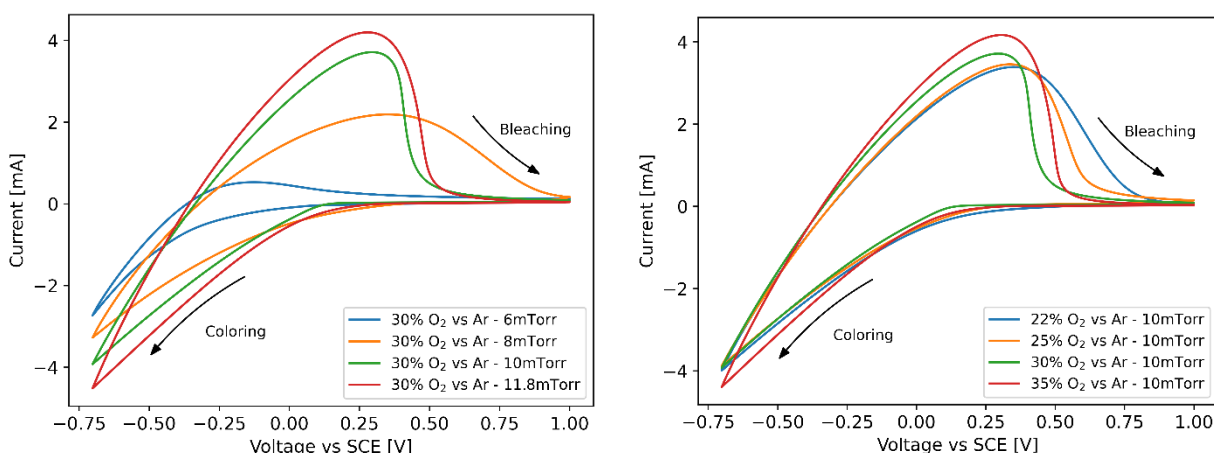


Figure 4.1: CV showing the impact of (left) the pressure and (right) the reactive gas concentration during deposition of the WO on its EC performance (5th cycle).

It is important to note that all the samples were stable over 30 cycles following an activation period which was only present for the first 4 cycles. The layer deposited at 6 mTorr showed a dark blue coloration in its as-deposited state due to a higher deposition rate and therefore, not enough O₂ (sub-stoichiometry). From Figure 4.1 and Table A-1 in the Appendix, which provides a quantitative summary of the samples' EC and optical performance, the pressure is shown to significantly impact

the EC performance of WO_3 . As explained in the Methodology section, the increase in pressure leads to a lower mean free path for the sputtered atoms, which results in a more porous layer being deposited onto the substrate. This creates more space for ion intercalation, which explains the improved EC performance at higher pressures.

Looking at the right-hand curves of Figure 4.1, the impact of the oxygen concentration during deposition is somewhat less pronounced as all four samples exhibit a similar behavior. However, the slope of the curve during the bleaching process correlates with the speed of the bleaching mechanism, indicating that the 35% O_2 vs Ar concentration appears to be more suitable than the others. When analyzing the packing density of the layer, the sample deposited at 35% O_2 vs Ar concentration has a packing density of 77.5% compared to the one deposited at 22% O_2 vs Ar concentration which has a packing density of 84.8%. These results are aligned with previous publications on the subject, describing that higher oxygen content and pressure enhance the EC performance of the layer, whereas lower values of these parameters lead to a metallic-like behavior with poor EC performance [90]. Hutchins *et al.* [91] demonstrated that insufficient oxygen content during deposition can result in an excess of oxygen vacancies. In comparison, increasing the oxygen concentration was shown to improve EC performance of the WO_3 film, until reaching a certain threshold closer to the stoichiometry of WO_3 . This minimizes the oxygen vacancies and thus decreases the number of W^{5+} sites, which are directly related to the absorption efficiency [92]. On the other hand, over-stoichiometric thin films have been shown to possess EC activity but such layers are immediately unable to revert to a transparent state once colored, resulting in the irreversibility of the EC phenomenon [93]. Consequently, the appropriate deposition conditions for the WO_3 layer were chosen to be at 10 mTorr with 35% O_2 vs Ar concentration.

Ion conductor optimization

Regarding the Ta_2O_5 coating, Tajima *et al.* [94] obtained a smoother surface with a DC-MS in comparison to RF magnetron sputtering. This leads to enhanced adhesion of the subsequent layers and provides better proton conductivity. The ion conductive layer has specific requirements for ion diffusion and needs to address potential short circuit issues; thus, the layer must be sufficiently porous and thick. To limit the propagation of defects, the deposition of Ta_2O_5 layers is conducted in two steps: after depositing half of the desired thickness, the shutter is closed for 5 min before

depositing the remaining thickness. The focus of this section is to determine the impact of the Ta_2O_5 layers under different deposition conditions on the EC performance of WO_3 . For this reason, different thicknesses and different densities were tested. The CV results are presented in Figure 4.2 below, where all the WO_3 layers were deposited under the optimized conditions determined above, aiming for a 350 nm thickness. The different Ta_2O_5 layers were prepared at room temperature with a magnetron power density of 9.87 W/cm^2 . Different thicknesses were tested with two distinct working pressures and gas mixtures: 4 mTorr with a 65% O_2 vs Ar concentration, and 7.5 mTorr with a 55% O_2 vs Ar concentration.

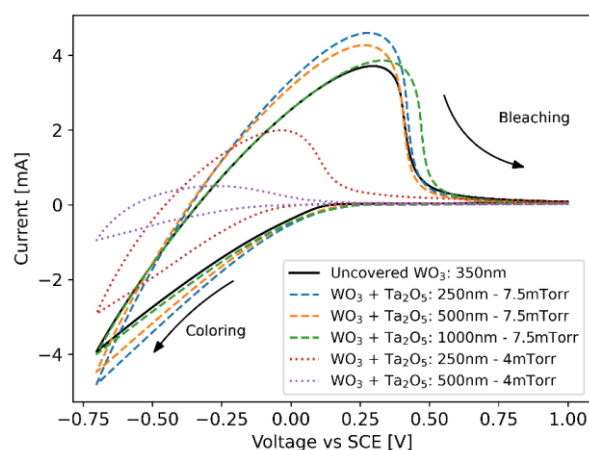


Figure 4.2: CV showing the impact of the Ta_2O_5 layer's porosity and thickness on the EC properties of a 350 nm WO_3 layer.

From these results, it becomes clear that the density of the ion conductor plays a crucial role in the EC performance of the WO_3 layer. Dense layers seem to inhibit charge insertion and extraction within WO_3 , as expected [95], which is not desirable for the fabrication of functional ASSDs. On the other hand, it was observed that increasing the thickness of the porous Ta_2O_5 layer results in a slight decrease in the EC performance, mainly due to an increase in the resistance of the material for charge insertion. Indeed, as evidenced from Table A-2 in the Appendix, the intercalation ratio decreases from 22.1% for the 250 nm porous Ta_2O_5 layer to 19.0% for the 1000 nm Ta_2O_5 layer. When comparing these two samples, the thicker layer also leads to $\sim 10\%$ drop in the transmission modulation, reducing it from 71.4% to 61.9%. Therefore, the porous layer's thickness must be

carefully chosen, to minimize short circuits while limiting its impact on the EC performance of the underlying WO_3 layer.

Optimization of the NiO layer's EC properties

The inclusion of vanadium in the Ni(93%)-V(7%) metallic target reduces the magnetic properties of the nickel, making it suitable for magnetron sputtering [96]. Multiple parameters were tested to promote the EC performance of the thin film as presented in Figure 4.3.

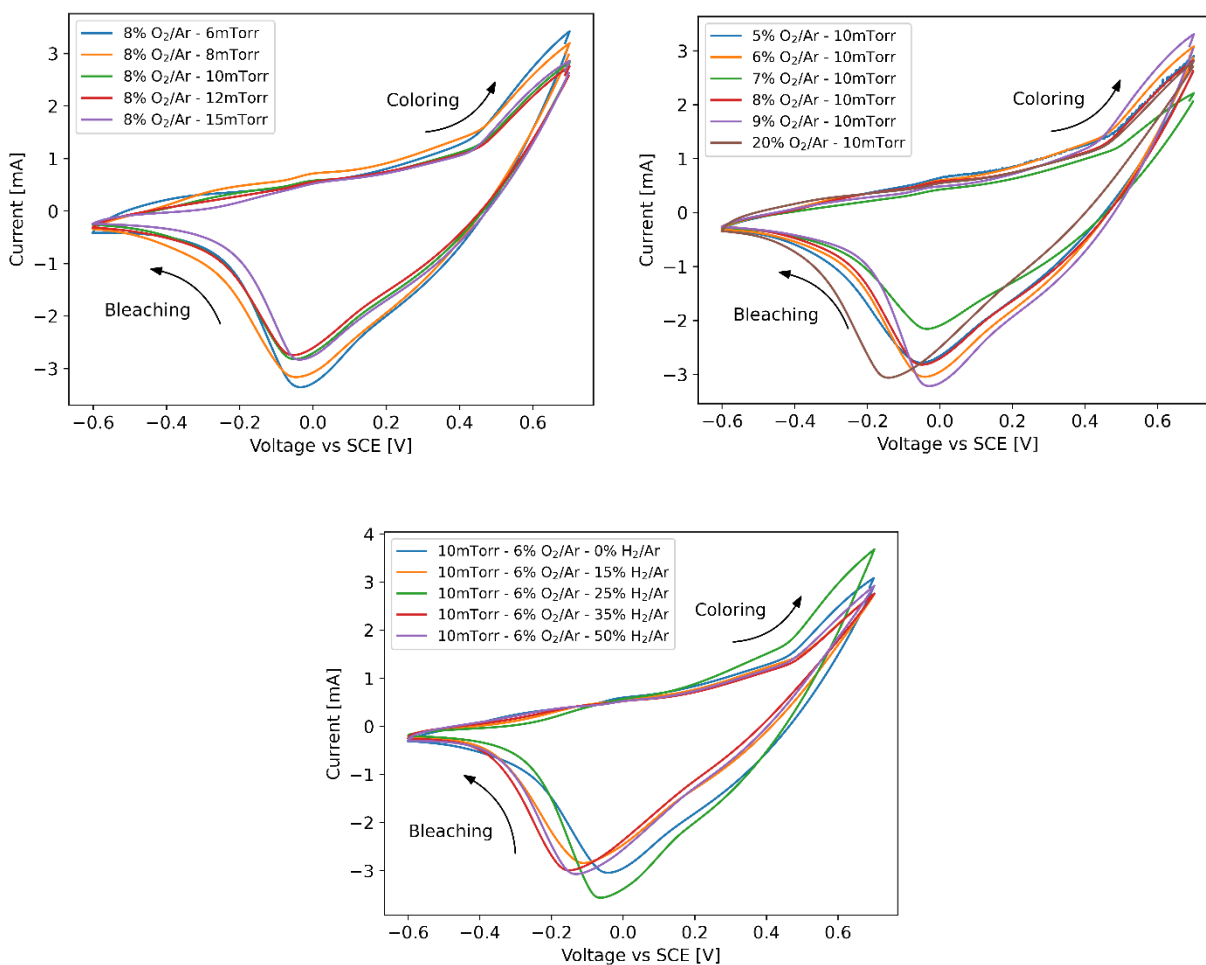


Figure 4.3: CV showing the impact of (top left) the pressure, (top right) the O_2 vs Ar concentration and (bottom) the H_2 vs Ar concentration during deposition of the NiO on its EC performance (20th cycle).

Initially, the pressure was varied while maintaining a constant 8% O₂ vs Ar concentration (arbitrary value). Then, the pressure was set at 10 mTorr to enable a wider range of reactive gas mixtures, while varying the O₂ vs Ar concentration. Finally, a last set of samples was deposited with the addition of hydrogen during the deposition, which allows to pre-intercalate H⁺ ions in the layer structure without using chemical solvents, while increasing the charge capacitance and transparency of the films [10, 26, 97]. For these samples, the pressure was kept at 10 mTorr with a constant 6% O₂ vs Ar concentration while varying the hydrogen concentration.

As expected from the NiO anodic EC behavior, the samples deposited without hydrogen (without proton intercalation) were brown in their as-deposited state, while the ones with the hydrogen gas mixture (pre-intercalated) appeared transparent with a slight yellowish tint. Unlike the WO₃ samples, the NiO layers required approximately 10 cycles to fully activate their EC performance, after which they demonstrated high stability over the following 20 cycles. Analyzing these results and referring to Table A-3 in the Appendix (which summarizes the EC and optical performance of each sample), it is difficult to point out a set of ideal conditions, as the different tests conditions led to a similar performance when considering the previously defined figure of merit. However, some conditions resulted in undesirable properties for an EC device. For instance, higher energies at lower deposition pressures led to an increase in the ion energy flux during deposition, resulting in larger surface roughness obtained by ellipsometry of around 40-50 nm, while the other conditions demonstrated a surface roughness of around 20 nm. Furthermore, although the sample deposited at 15 mTorr displayed the best intercalation ratio (22.3%) with the lowest packing density (47.4% compared to 57.3% for the sample deposited at 12 mTorr), it did not achieve as high of a hydrogen concentration during the deposition as the sample deposited at 10 mTorr due to limitations in the system's working pressure.

The addition of H₂ during the deposition of NiO appeared to offer the best transmission modulation at 550 nm and coloration efficiency among all the samples, particularly the sample with 25% H₂ vs Ar concentration, which exhibited the lowest packing density (81.0%) compared to other hydrogen-deposited samples. In addition, to justify the final choice of the deposition conditions for NiO, the evolution of the ionic diffusion coefficient and the intercalation ratio over the 30 cycles are presented in Figure 4.4.

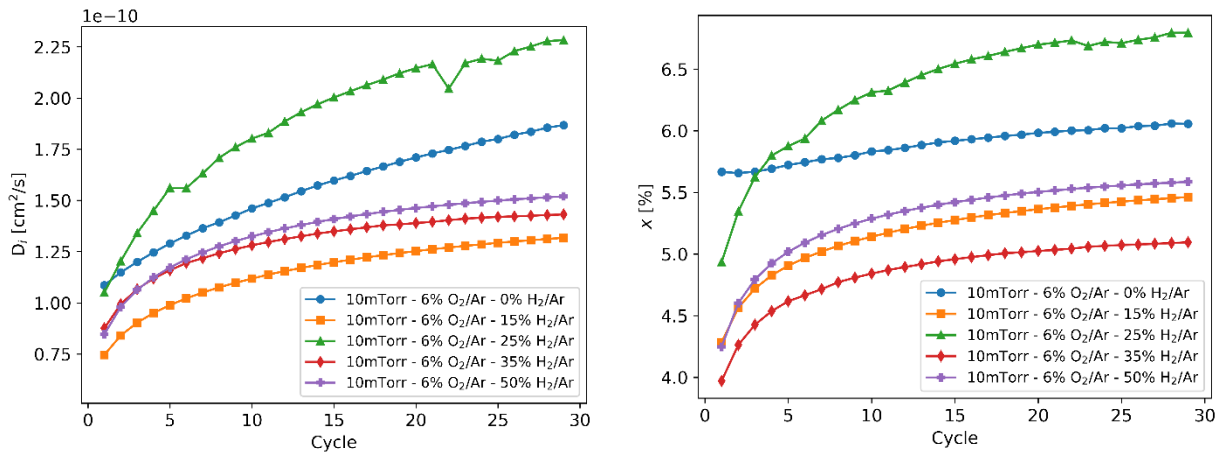


Figure 4.4: Evolution of (left) the ionic diffusion coefficient and (right) the intercalation ratio over the 30 cycles for the hydrogen-deposited samples.

It is worth noting the first cycles of EC activation, where the properties increase over the first 10 cycles, before stabilization. Among all the samples deposited with hydrogen, the one with a 25% H_2 vs Ar concentration exhibited superior properties over time. Furthermore, this approach provides a significant advantage in the fabrication of ASSDs. The ability to pre-intercalate protons during deposition [98] may eliminate the need for chemical pre-intercalation in the WO_3 layer. This would not only facilitate the fabrication process but would also reduce the probability of introducing particles or defects from the ambient air and the manipulation of the sample (which will be further investigated in detail in Section 4.3).

Top electrode optimization

Finally, an ITO thin film is used as the top transparent electrode in the ASSDs. The deposition conditions must be chosen carefully as the layer needs to be conductive enough (low resistivity ρ) to ensure the uniformity of the coloration of the devices and provide fast coloration and bleaching kinetics, while maintaining a high transparency [99]. Previous publications showed that the choice of deposition conditions plays a major part in the properties of the ITO thin film: switching from DC to RF magnetron sputtering allows for a higher transmission albeit at a lower deposition rate [100], and decreasing the working pressure to densify the film [101] or increasing the thickness

[102] enhances the conductivity. In this work, the sheet resistance was obtained from a contactless probe. The resistivity can then be calculated by multiplying the sheet resistance by the thickness of the coating. A comparison of four ITO samples was performed, with two samples deposited at a working pressure of 10 mTorr and two at 1 mTorr. Each pressure condition was tested using both DC and RF magnetron sputtering, with pure Ar gas and a power density of 2.19 W/cm^2 for 20 minutes. Table 4-1 highlights the impact of the pressure and the type of magnetron sputtering on the luminous transmission (T_{lum}) and resistivity (ρ).

Table 4-1: Comparison of the ITO's T_{lum} and ρ according to the deposition conditions.

	DC magnetron sputtering	RF magnetron sputtering
10 mTorr	Thickness: 77 nm $T_{lum} = 76.1\%$ $\rho = 1.5 \times 10^{-5} \Omega.m$	Thickness: 42 nm $T_{lum} = 80.0\%$ $\rho = 6.1 \times 10^{-5} \Omega.m$
1 mTorr	Thickness: 92 nm $T_{lum} = 68.9\%$ $\rho = 1.9 \times 10^{-5} \Omega.m$	Thickness: 44 nm $T_{lum} = 75.7\%$ $\rho = 7.4 \times 10^{-6} \Omega.m$

Some studies show that the thickness of ITO is expected to decrease its T_{lum} [103], thus, the experimental values obtained here are inconclusive when comparing layers obtained by DC and RF sputtering. However, Anandan *et al.* [100] demonstrated an increase in transmission from DC to RF magnetron sputtering for similar thicknesses. Indeed, the lower deposition rate from RF sputtering reduces the presence of defects (source of scattering) in the material by improving its crystallinity. On the other hand, lower pressures during deposition lead to higher energetic bombardment of the sputtered atoms, further enhancing the crystallinity [101]. In other words, reducing the working pressure enhanced the conductivity (lower resistivity) of the ITO film, as observed experimentally. Consequently, the ITO deposited at 1 mTorr with RF sputtering was selected as the top transparent electrode of the ASSD.

A final test was performed to characterize the EC performance of this material. For this purpose, both CV tests and *in-situ* transmission measurements were performed on two samples: an

uncovered commercial ITO substrate as well as on a 150 nm ITO layer deposited on a commercial ITO substrate (see Figure 4.5). These tests were performed using the same methodology as employed for the WO_3 layer characterization.

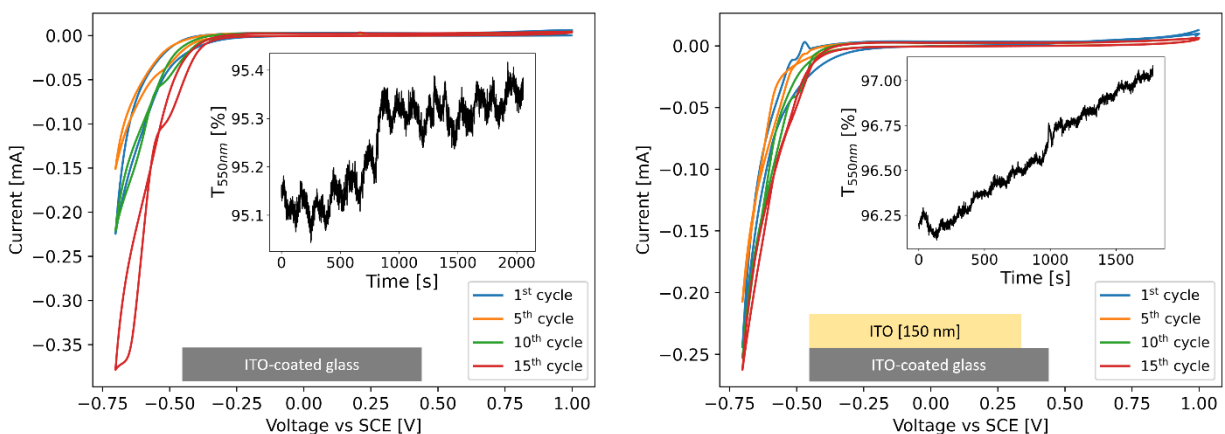


Figure 4.5: CV and *in situ* transmission at 550 nm over time for (left) an uncovered ITO-coated glass from Delta Technologies and (right) a covered substrate with a 150 nm ITO deposited film.

These results indicate that both the commercial ITO substrate and the deposited ITO layer exhibit limited EC activity, as shown by the minimal variation of the transmission at 550 nm after 15 cycles and minimal current variation. This current variation could be due to side reactions of the ions in the liquid electrolyte. Thus, it is possible to conclude that the ITO films are stable and do not contribute to the overall activity of the EC films.

4.2.2 Comparison of the EC performance between WO_3 and NiO

The performance of the EC materials deposited with the final conditions described in the Methodology section is shown in Figure 4.6. The high stability of WO_3 is demonstrated by its consistent performance over time, while NiO shows a slower activation process with the need for several cycles to fully activate its EC activity. Their complementary behavior (respectively cathodic and anodic) can be observed with their reversed duck-shape CV curves showing that the WO_3 colors with negative potentials while the NiO colors with positive potentials.

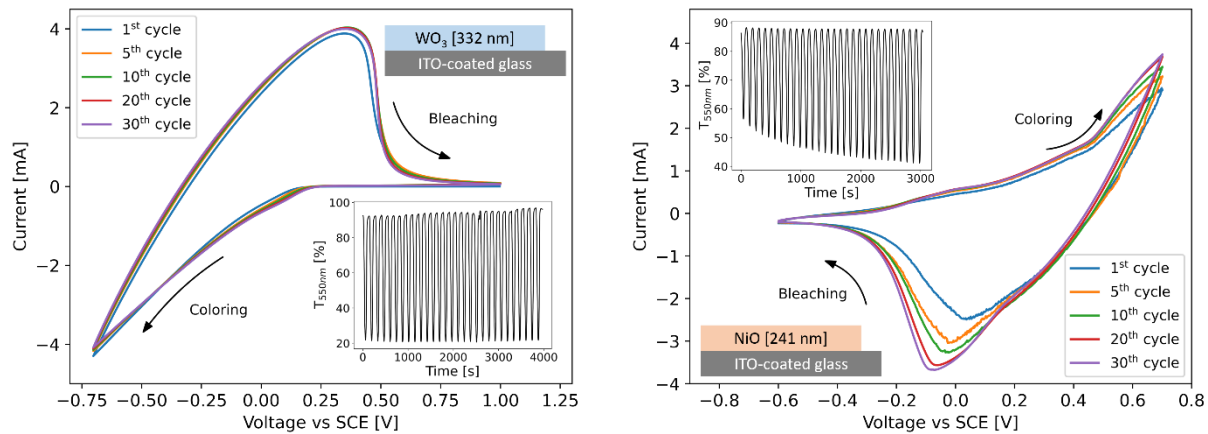


Figure 4.6: CV over 30 cycles and *in situ* transmission at 550 nm for (left) a 332 nm WO₃ layer immersed in a 0.1 mol/L H₂SO₄ electrolyte and (right) a 241 nm NiO layer immersed in a 1 mol/L KOH electrolyte.

The above figure can be supplemented by Table 4-2 which highlights the main characteristics of both EC materials. A disparity in the ion diffusion coefficients (D_i) can be observed between the WO₃ and NiO, with a difference of two orders of magnitude, which could potentially impact the overall device coloration and bleaching dynamics. The transmission modulation at 550 nm (ΔT_{550nm}) also presents a contrast between the two EC materials, suggesting that the NiO is unable to achieve as low a level of coloration as WO₃ at the specified wavelength. The choice of 550 nm as the reference wavelength is based on the fact that it corresponds to the peak sensitivity of the human eye. However, it is important to note that NiO absorbs more in the blue region of the visible spectrum.

Table 4-2: Main EC and optical performance of the two EC materials (20th cycle).

	WO ₃ (332 nm)	NiO (241 nm)
D_i [cm ² /s]	2.9×10^{-8}	2.2×10^{-10}
ΔT_{550nm} [%]	68.7	47.9
η_{550nm} [cm ² /C]	85.3	87.7

The literature reports a range of ionic diffusion coefficients for WO_3 , typically varying from $10^{-9} \text{ cm}^2/\text{s}$ to $10^{-12} \text{ cm}^2/\text{s}$ [104], and around $10^{-12} \text{ cm}^2/\text{s}$ for NiO [26]. Therefore, the layers obtained with the chosen deposition conditions exhibit excellent proton diffusion capabilities, since the results obtained are higher than the values published in the literature. The transmission modulation and coloration efficiencies also align quite well with the values reported in the literature [33, 105].

Despite having a similar coloration efficiency, NiO exhibits a lower ionic diffusion coefficient compared to WO_3 . This can be considered an issue regarding charge balancing and charge trapping between the two EC materials, particularly in the context of fabricating functional ASSDs. This will be investigated in the next subsection which examines the coloration properties of both materials and investigates their ability to insert and extract charges at various intercalation levels.

4.2.3 Obtaining tailored optical properties of the EC materials

In order to understand the coloration mechanism of the EC materials and predict the optical response of the final ASSDs, it is crucial to characterize the different coloration levels of the WO_3 and NiO coatings individually. The methodology involved applying specific potentials to obtain their bleached states and different levels of coloration based on the following steps:

1. Obtaining the bleached state: a potential of 1 V was applied for WO_3 in a 0.1 mol/L H_2SO_4 solution and a potential of -0.6 V for NiO in a 1 mol/L KOH solution for 1 min to obtain the most bleached state possible.
2. Obtaining intermediate levels of coloration: the potential was switched from 1 V to -0.1 V for WO_3 and from -0.6 V to 0.1 V for NiO with a constant scan rate of 25 mV/s, before applying the desired potential for 2 min, to ensure saturation at the desired coloration level.
3. Characterization: the samples were rinsed with DI water and dried with a nitrogen gun before being characterized by ellipsometry and spectrophotometry within 1 min after applying the desired potential to minimize coloration loss due to self-bleaching.
4. Finally, the methodology is repeated for the set of chosen potentials as described in Table 4-3.

Table 4-3: Coloration characterization methodology for both EC materials.

Material	Bleached state Colored state				
WO ₃	+1.0 V	-0.1 V	-0.3 V	-0.5 V	-0.7 V
NiO	-0.6 V	+0.1 V	+0.3 V	+0.5 V	+0.7 V

However, all samples that were colored with this methodology exhibited a significant loss in transmission after the characterization step. This was due to the self-bleaching of the samples as the protons are able to leave the layers. As a result, all the coloration characterizations were performed with an additional Ta₂O₅ layer on top of the EC material. Indeed, this helped to mimic the final design of the ASSD while protecting the EC layer during the CV in the acid (or basic) solution. It also helped stabilize the EC material's colored state resulting in a decrease in the self-bleaching of the sample over time.

The self-bleaching behavior of a 350 nm WO₃ layer both uncovered and covered by a 250 nm Ta₂O₅ layer was characterized by applying an open-circuit potential (OCP) after obtaining the different coloration levels while measuring the *in situ* transmission for 10 min. The uncovered WO₃ layer exhibited up to 18% increase in its transmission after coloration at -0.3 V while it only increased by 0.6% for the covered WO₃ sample. For the most colored state, a 4.6% transmission increase was observed for the uncovered layer compared to 1.6% for the one covered with Ta₂O₅. This highlights the importance of the protective Ta₂O₅ layer when performing *ex situ* characterization. Thus, it ensures a more accurate and reliable characterization of the EC materials' different coloration levels.

Another CV test with *in situ* transmission measurements was conducted in order to assess the impact of the protective Ta₂O₅ layer on the performance of the EC material (see Figure 4.7). Considering that the addition of Ta₂O₅ leads to more optical interference fringes in the transmission spectra, the luminous transmission T_{lum} was used - as it considers the whole visible spectrum - to compare the coloration evolution over time for both the WO₃ and NiO samples, both uncovered and covered by a Ta₂O₅ layer.

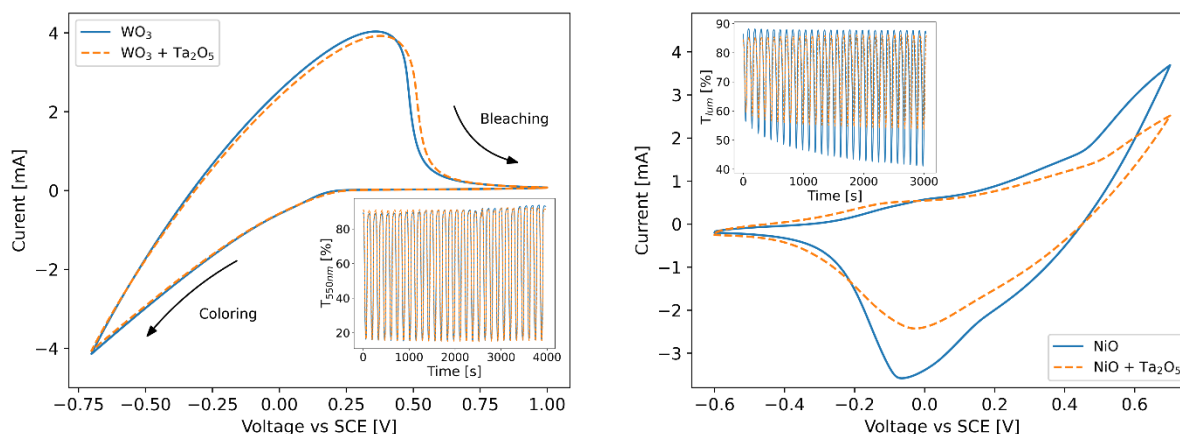


Figure 4.7: Impact of the Ta₂O₅ layer on the coloration study of the (left) WO₃ and (right) NiO's EC and optical performance (20th cycle).

While the presence of the Ta₂O₅ layer has a minimal impact on the performance of the WO₃ layer, it is quite obstructive for the NiO layer. The addition of the Ta₂O₅ on top of the NiO layer alters both its optical and EC performance, reducing the ion diffusion coefficient from $1.8 \times 10^{-10} \text{ cm}^2/\text{s}$ to $8.3 \times 10^{-11} \text{ cm}^2/\text{s}$, the intercalation ratio from 3.6% to 2.8% and the luminous transmission modulation from 45% to 32% (considering the 20th cycle). One possible explanation is that the Ta₂O₅ layer was specifically optimized for proton diffusion in an H₂SO₄ electrolyte, while the CV for NiO was performed in a KOH electrolyte. Hence, the observed alteration in EC performance may be attributed to the migration of OH⁻ ions instead of H⁺ ions. This must be kept in mind when characterizing the coloration states of the NiO as it adds uncertainty regarding the achieved level of intercalation. It is important to note that the scan rate chosen in the CV recipe may impact the observed performance, as increasing the time for intercalation would allow for more ions to be intercalated into the materials' microstructure. Hence, the coloration characterization methodology described above involves applying the desired potential for 2 minutes, which provides a more representative assessment of the NiO coloration performance even with the presence of the Ta₂O₅ layer. Figure 4.8 presents the increasing number of charges inserted in the EC layers upon their coloration.

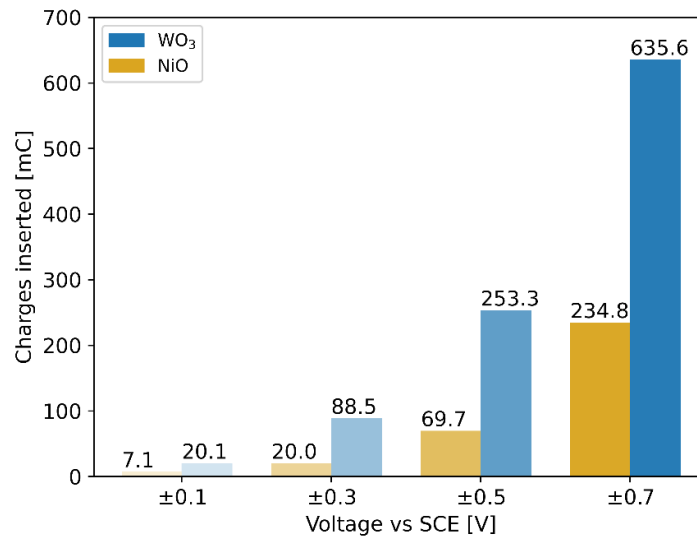


Figure 4.8: Evolution of the number of charges inserted into the EC materials upon coloration.

The significant disparity observed between the two EC materials can be attributed to multiple factors. As mentioned earlier, the Ta₂O₅ layer on top of the NiO film causes the inhibition of inserted charges, which explains the decrease in its performance compared to the WO₃ sample. Another important factor to consider is the difference in the electrolyte solutions as explained before. The chemical reactions involved in the coloration and bleaching processes of the NiO are still not completely understood in the scientific community (see Section 2.2.2). However, as the addition of the Ta₂O₅ layer replicates part of the standard architecture of an ASSD, these observations can still be relevant for the final device performance modeling. Yet, the ASSDs developed in the next section function with intercalation/deintercalation of protons. Thus, the predicted optical properties for the NiO might be different in the context of an ASSD. In addition, the NiO microstructure may not be able to intercalate the same quantity of ions present in the WO₃ layer without charge trapping. Thus, it is important to carefully control the quantity of ions inserted into the NiO layer to maintain a high inserted versus extracted charge ratio.

Following the assessment of the EC performance of both materials, it is also interesting to assess their optical behavior in the bleached and most colored states as presented in Figure 4.9 and Figure 4.10. They summarize the WO₃ and NiO's refractive index (n) and extinction coefficient (k) as

well as their reflection, transmission and absorption in the visible spectrum. The calculated RGB colors are also presented.

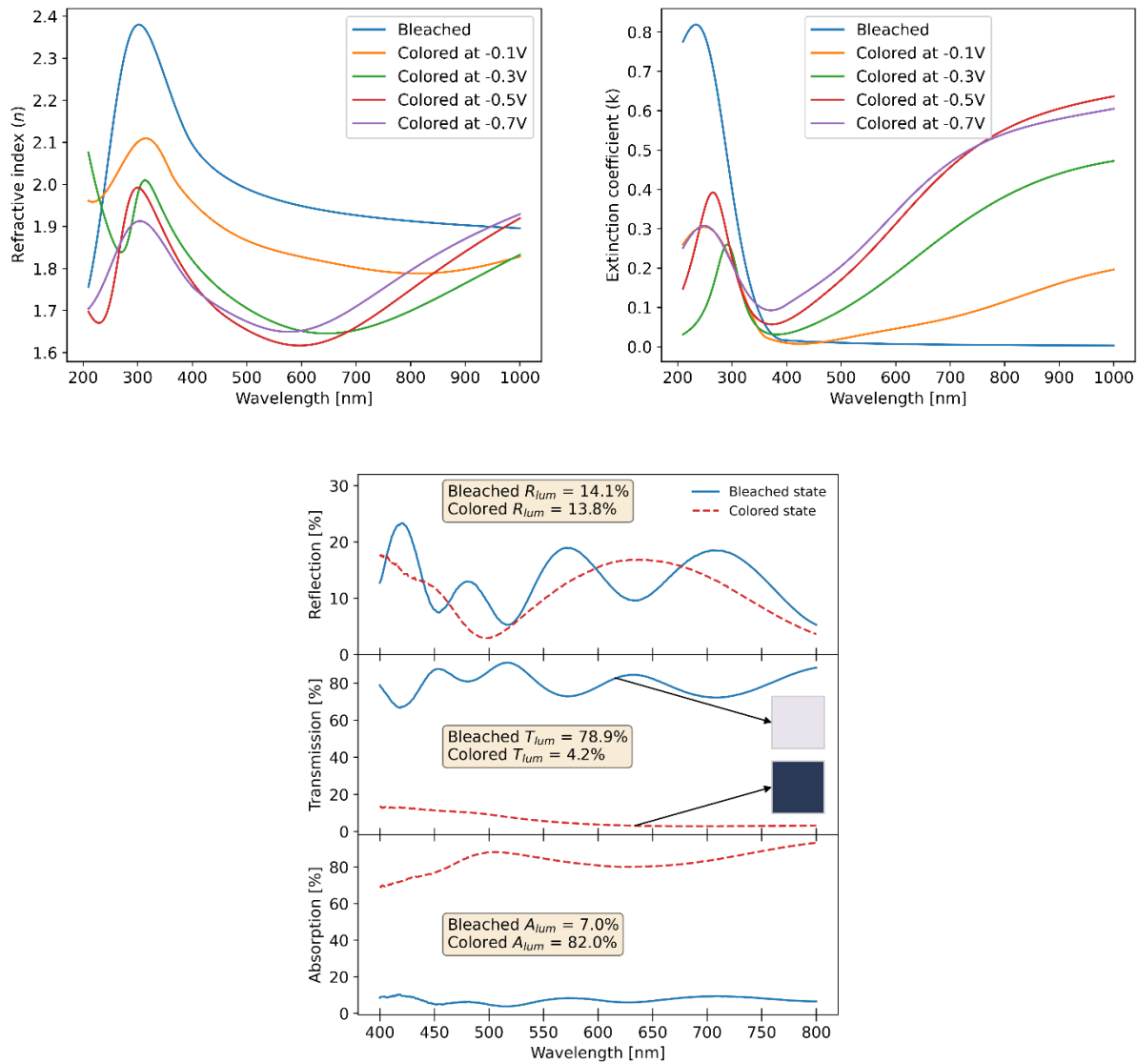


Figure 4.9: (Top left) Refractive index, (top right) extinction coefficient for the different coloration levels, and (bottom) reflection, transmission, and absorption for the bleached and most colored states of a WO_3 layer covered with a 250 nm Ta_2O_5 layer.

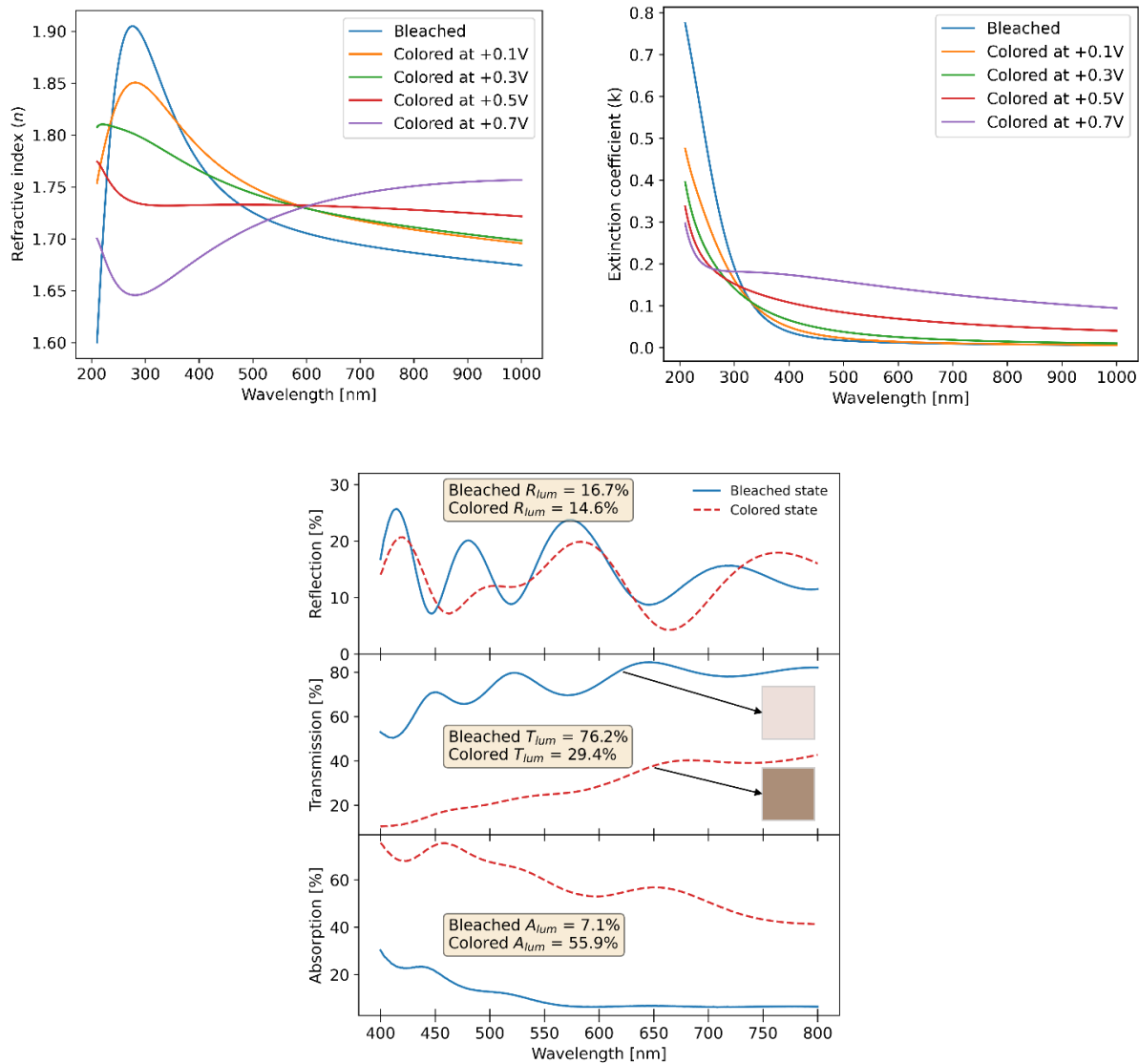


Figure 4.10: (Top left) Refractive index, (top right) extinction coefficient for the different coloration levels, and (bottom) reflection, transmission, and absorption for the bleached and most colored states of a NiO layer covered with a 250 nm Ta_2O_5 layer.

As expected, both the WO_3 and NiO EC materials exhibit a large transmission and absorption modulation upon coloration. For the WO_3 , the T_{lum} shows a considerable change of 74.7%, while the A_{lum} demonstrates a change of 75.0%. Similarly, the NiO presents interesting variations with a ΔT_{lum} of 46.8% and a ΔA_{lum} of 48.8%. In terms of reflection, both materials present a decrease upon

coloration, with a small variation of $\Delta R_{lum} = -0.3\%$ for WO_3 and a more marked reflection modulation of -2.1% for NiO . In addition to the above results, Table 4-4 summarizes the refractive indices and extinction coefficients of all the materials deposited with the conditions determined in their bleached and most colored states.

Table 4-4: Optical properties of the materials in their bleached and most colored states used to fabricate the ASSDs.

		Refractive index at 550 nm (n)	Extinction coefficient at 550 nm (k)
WO_3	<i>Bleached</i>	1.97	8.26×10^{-3}
	<i>Colored</i>	1.65	2.70×10^{-1}
Ta_2O_5		2.11	$< 10^{-4}$
NiO	<i>Bleached</i>	1.71	1.36×10^{-2}
	<i>Colored</i>	1.75	1.50×10^{-1}
ITO		2.09	1.30×10^{-2}

All of the investigated materials seem to exhibit a low absorbance in their bleached state due to their low extinction coefficients, which is beneficial for fabricating ASSDs for ophthalmic applications.

4.3 Fabrication of the improved architecture

4.3.1 Cleaning procedure efficiency

As outlined in the Methodology section, the cleaning procedure for the substrate prior to the fabrication of the ASSD plays a major role in avoiding short circuits, and thus for its proper functioning. To illustrate the performance of the cleaning process, Figure 4.11 shows pictures using an optical microscope (x40) of the edge of a substrate before (the as-bought commercial ITO-coated substrate) and after the cleaning procedure (see Section 3.2.2 for more details).

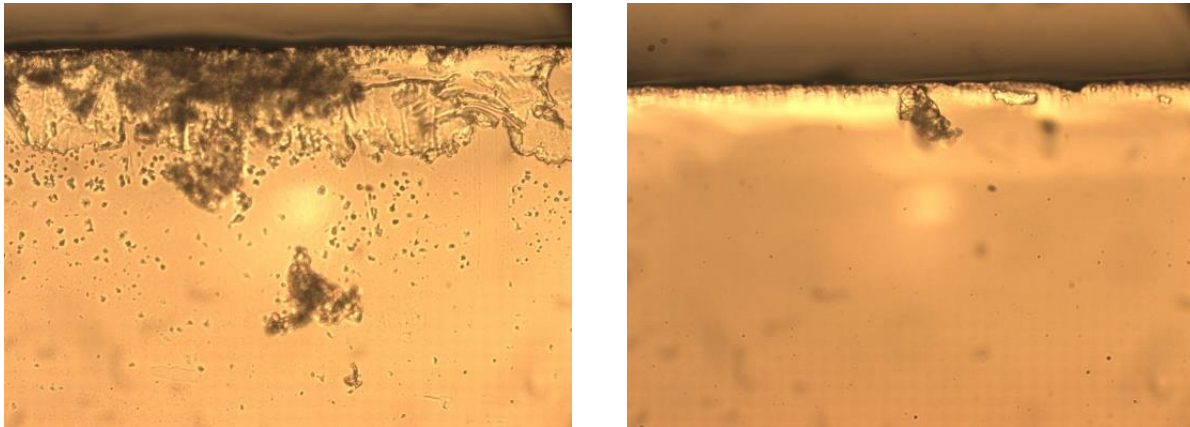


Figure 4.11: Pictures from an optical microscope (x40) of the edge of a substrate (left) before and (right) after the cleaning procedure.

In the images shown above, only the edges of the substrates are presented, as the dirt is effectively removed from the remaining parts of the substrate during the cleaning procedure. The picture on the right in Figure 4.11 highlights the presence of residual dirt on the edges of the substrate left after the cleaning process. This could be due to the handling and manipulation of the substrate between each step of the procedure. Therefore, this cleaning procedure is not sufficient to prevent the presence of residual dirt. Consequently, additional steps are needed during the ASSD fabrication to ensure a more reliable and repeatable methodology.

4.3.2 Optimized ASSD fabrication procedure

Figure 4.12 presents the optimized fabrication process that ensures the proper functionality for all subsequent ASSDs produced following this methodology. A plasma etching treatment was initially performed on the ITO substrate to remove the material from the edges (red stripes in Figure 4.12) before the deposition of WO_3 and Ta_2O_5 . The plasma etching treatment is performed by applying a bias of 100 W for 15 minutes at a working pressure of 10 mTorr and a gas mixture of 50% H_2 vs Ar concentration. Then, a Kapton mask was applied to reduce the deposition area of the NiO and the top ITO (black stripe in Figure 4.12), and therefore get rid of the substrate's edges. The efficiency of these new steps will be studied afterward (see Section 4.3.3). To optimize the functionality of the fabricated ASSDs, the deposition of ITO on the NiO layer also needs to be

addressed. It has been observed that depositing the top ITO film onto a rough surface can lead to an increase in its resistivity [106]. However, it has also been previously established that the NiO layer exhibits a surface roughness of approximately 20 nm (see Section 4.2.1). Hence, a plasma treatment was incorporated to smoothen the NiO surface by applying a bias of -130 V at a working pressure of 19 mTorr, using pure argon for 15 minutes. As a result, the surface roughness was reduced to less than 2 nm.

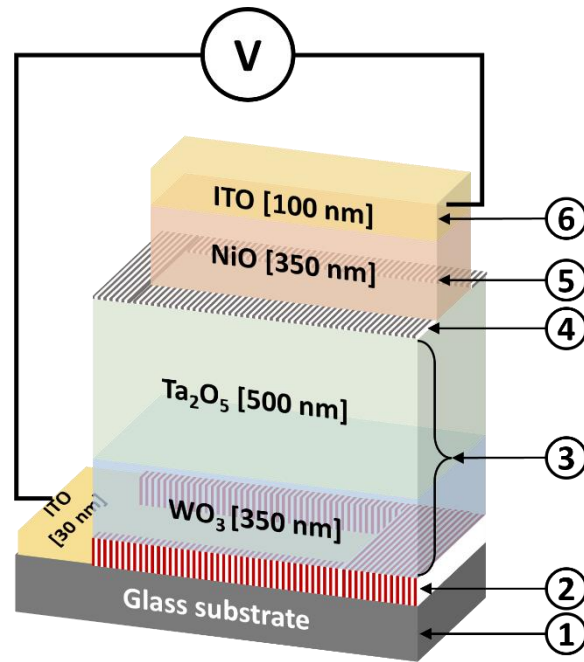


Figure 4.12: Optimized architecture of the ASSD. (1) cleaning procedure, (2) plasma etching of the substrate, (3) deposition of WO_3 and Ta_2O_5 , (4) reduction of the deposition area with a Kapton mask, (5) deposition of NiO and plasma treatment of its surface, and (6) deposition of ITO.

The deposition procedure can be segmented into six major steps listed as follows:

1. Cleaning of the substrate as described in Section 3.2.2.
2. Etching the edges of the ITO-coated glass substrate to prevent any defects from the edges and any contact with the upper electrode.

3. Application of a plasma treatment to remove any residual organic residue followed by the deposition of the WO_3 and Ta_2O_5 layers.
4. Removal of the sample from the deposition system to apply a Kapton mask on the deposited coatings to reduce the deposition area for the subsequent layers.
5. Deposition of the NiO layer with hydrogen to pre-intercalate the charges and application of a plasma treatment to smoothen the surface of the coating.
6. Deposition of the top ITO layer.

The insertion of protons in the ASSDs can be performed either electrochemically or during the deposition of the EC materials and will be addressed at the end of this chapter (see Section 4.3.4). Finally, the potential is established between the top and bottom ITO electrodes to enable the displacement of ions within the device, resulting in the coloration and bleaching of the overall ASSD. By incorporating these refinements, the risk of short circuits is minimized, solving the main issue encountered at the FCSEL for fabricating ASSDs over the past decade. With the incorporation of the cleaning procedure and the optimized fabrication methodology, all devices were successfully functional without any visible self-bleaching. Hence, the overall procedure is efficient and reproducible. In addition, the thickness of the final top ITO has been a limiting factor for previous work on ASSDs [8]. Indeed, the ASSDs with a top ITO layer thicker than 30 nm favored the presence of short circuits. However, the aforementioned procedure enabled to get rid of these issues, hence allowing for a thicker, and thus more conductive, ITO electrode. The fabrication of reproducible functional ASSDs made it possible to perform the characterization of the devices' EC and optical performance and focus on its overall optimization. This will be performed in the next chapter.

4.3.3 Impact of the substrate's edges removal

Figure 4.13 compares the initially implemented ASSD fabrication method for a Glass / ITO / WO_3 / Ta_2O_5 / NiO / ITO basic architecture with the final optimized methodology (previously detailed) to prevent short circuits. Samples were fabricated with both methodologies and fully colored to observe the presence of self-bleaching.

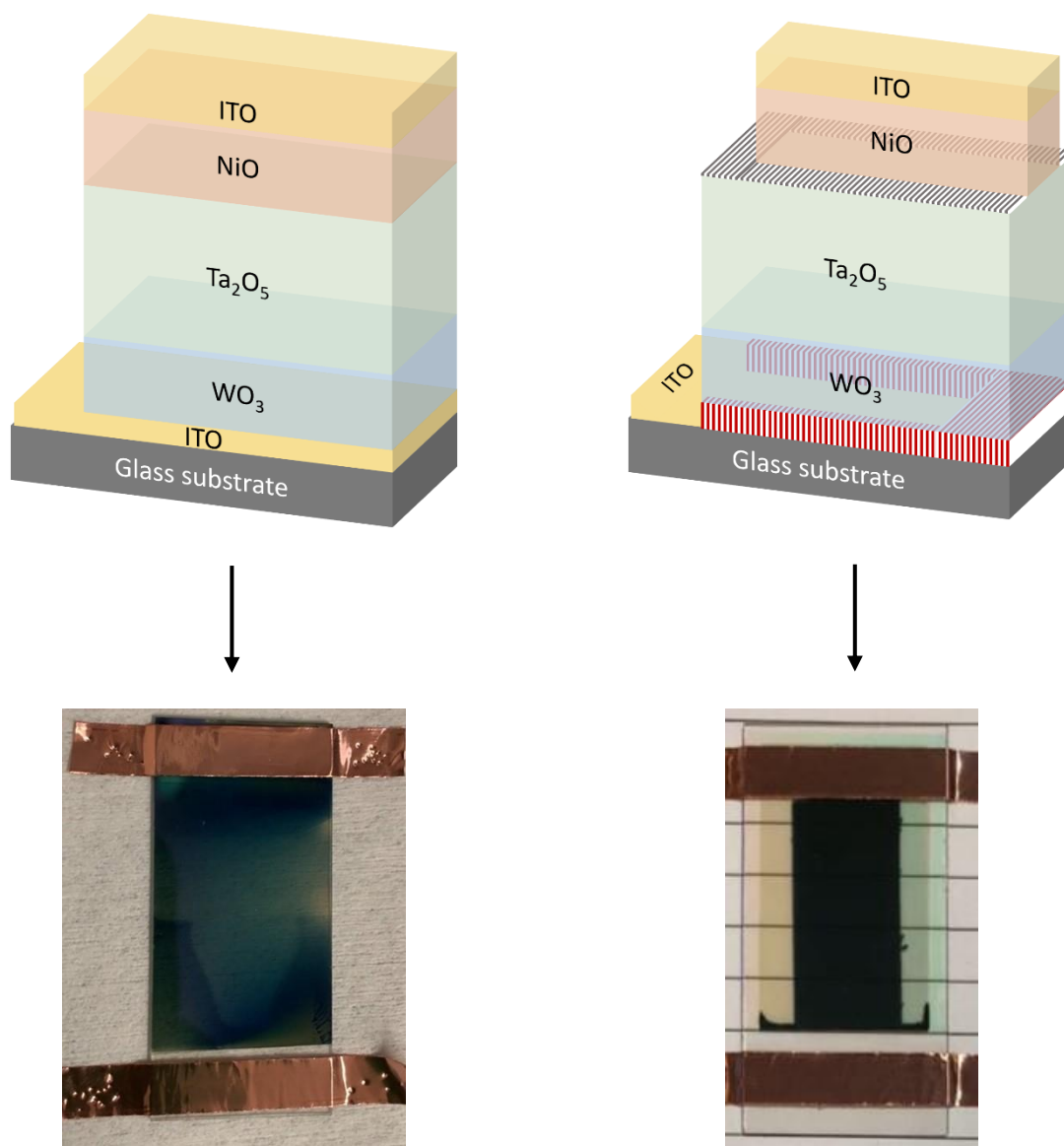


Figure 4.13: (Left) Fabrication of a basic ASSD structure and (right) the optimized fabrication methodology to get rid of the self-bleaching issues. The pictures were taken 10 seconds after stopping the current application.

The pictures taken 10 seconds after stopping the current application show a rapid and intense self-bleaching all over the left sample, with more transparency noticeable on the edges. Based on this observation, the discoloration is likely due to the presence of residual dirt or impurities that were not completely removed from the edges during the cleaning procedure. In contrast, the device on

the right does not display any clear visual self-bleaching even after several minutes. Thus, the addition of a thorough cleaning procedure along with an optimized fabrication methodology resulted in a more uniform and stable ASSD performance. The appearance of colored bottom wings on the right picture of Figure 4.13 results from the diffusion of ions through the area of the device that is on top of the etched bottom ITO surface. This area of the device is represented by the layers covering the red stripes in the corresponding architecture of the figure. These wings remain colored even after attempting to bleach the device. This phenomenon indicates that some protons are trapped and do not actively participate in the subsequent coloration and bleaching processes, thus decreasing the total amount of ions participating in the proper functioning of the ASSD. To mitigate this issue in future ASSDs, the difference between the areas of the two electrodes should be minimized. In other words, in the right architecture of Figure 4.13 the areas represented by the red and black stripes should be comparable.

4.3.4 The effect of pre-intercalation in the ASSD

Another crucial challenge in the reproducibility of the ASSDs fabrication is the pre-intercalation of H^+ ions in the devices. One possibility is to electrochemically pre-intercalate the protons in the WO_3 layer before depositing the subsequent layers. Since the addition of a Ta_2O_5 protective coating on the WO_3 has been shown to minimize the loss of charges over time, this step has been tested as an interesting solution. However, the insertion of the sample into an acid solution does not allow for a proper drying and cleaning procedure before reinstalling the sample into the deposition system for the rest of the ASSD fabrication process. Furthermore, as shown during the characterization of the EC materials' coloration states (see Section 4.2.3), the intercalation level which can be reached in NiO is lower than in WO_3 . This would increase the risk of overcharging in the NiO, resulting in a degradation of its EC performance. However, it was shown before, while choosing the ideal deposition conditions for NiO, that it is possible to pre-intercalate the H^+ ions during deposition. This approach allows using only the ions encapsulated in the device during the deposition of the NiO layer.

One major issue to be addressed in the next chapter is the difficulty to predict the intercalation levels of the EC materials, as it makes the process of establishing the amount of inserted or extracted charges significantly harder. To address this aspect, two ASSDs were fabricated: one

with the chemical pre-intercalation of ions in the WO_3 layer (while still depositing NiO with H_2), and the other only using protons from the NiO deposition. Their optical performance is presented in Figure 4.14, which shows the *in situ* transmission at 550 nm, with a focus on the 5 first and 5 last cycles during a total of 100 cycles of coloration and bleaching obtained by applying -3 V and +3 V, respectively, for 1 min each.

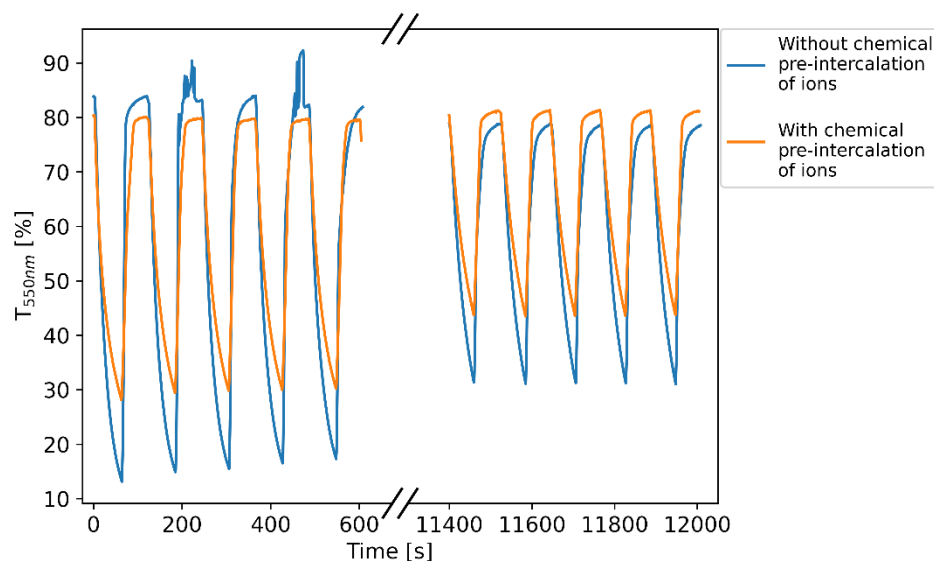


Figure 4.14: Comparison of the transmission at 550 nm for the first 5 cycles versus the last 5 cycles after a total of 100 cycles between ASSDs with and without chemical pre-intercalation of ions in the WO_3 layer.

Figure 4.14 highlights the higher transmission contrast between the bleached and colored states of the ASSD without the chemical pre-intercalation. It is also important to notice that both ASSDs show a degradation of the colored state vs cycling which is most probably due to charge trapping in the NiO layer that reduces the amount of available reversible intercalation sites. Indeed, if the colored state of the device degrades over time, it is likely related to charge trapping in the anodic material (NiO), as it colors upon deintercalation. On the other hand, if the transmission corresponding to the bleached state decreases over time, it suggests that charge trapping is occurring in the WO_3 layer due to its cathodic EC behavior.

Understanding the presence of charge trapping in the EC layers is crucial, as it offers valuable insights into improvements in the device design. Another important consideration for omitting the chemical pre-intercalation of ions is to facilitate the overall fabrication process, especially with regards to potential industrialization. Such a methodology would prevent the need for chemical compounds, thus minimizing the impact on the microstructure of the films (and the environment), as well as facilitating the scalability of the process. Finally, it is worth mentioning that previous studies have explored the pre-intercalation of H^+ ions during the deposition of WO_3 as well [107]. However, to ensure charge balancing between both EC materials, this avenue has not been explored in this project.

CHAPTER 5 ASSESSMENT OF THE ASSD PERFORMANCE

5.1 Foreword

This chapter summarizes the performance of the functional ASSDs fabricated in accordance with the cleaning procedure and fabrication methodology previously developed. It presents the results aimed at fulfilling the main objectives of this project, which are to obtain an AR ASSD in the bleached state, maximize the transmission modulation upon coloration with a minimum reflection increase of 10%, and finally, characterize the durability and long-term stability of the device. It also highlights the difficulty in predicting the optical response with modelling, especially concerning the colored state of the ASSDs. Finally, it shows the first results obtained for an ASSD fabricated on Essilor polymer substrates used for industrial lens applications.

5.2 Assessment of the transmission modulation

The transmission modulation may be controlled by adjusting the thickness of the different films in the ASSD. Increasing the thickness of the EC material leads to higher charge storage capacity, hence to higher transmission modulations [108, 109]. In addition, according to the Beer-Lambert law, the transmission decreases exponentially with thickness in the context of an absorbing material, indicating that thicker WO_3 or NiO layers lead to higher absorption. However, choosing the appropriate thickness of the material is also important from an EC point of view. Indeed, Kim *et al.* [110] have shown that there are three possible intercalation sites in the EC materials microstructure: active reversible sites, reversible trap sites with a possible galvanostatic rejuvenation to retrieve the EC performance [60], and irreversible deep trap sites that lead to non-desired residual absorption over time. Therefore, the appropriate thickness is limited by the occurrence of charge trapping, meaning that a too thin EC material leads to difficulties in recovering its fully bleached state after several cycles as the probability to reach these non-reversible sites increases [111]. All the studied subsequent ASSDs were fabricated with both EC materials having a thickness of 350 nm.

The ion conductor's thickness can also have a significant impact on the device transmission modulation, as described in the previous chapter. Hence, four ASSDs fabricated with different

Ta₂O₅ thicknesses, 250 nm, 500 nm, 750 nm and 1000 nm, were characterized over 100 cycles of coloration/bleaching (switching between +/- 3 V), as illustrated in Figure 5.1. The chronoamperometry over the first three cycles, the T_{lum} for the first three and last three cycles and the response times over time are shown for comparison.

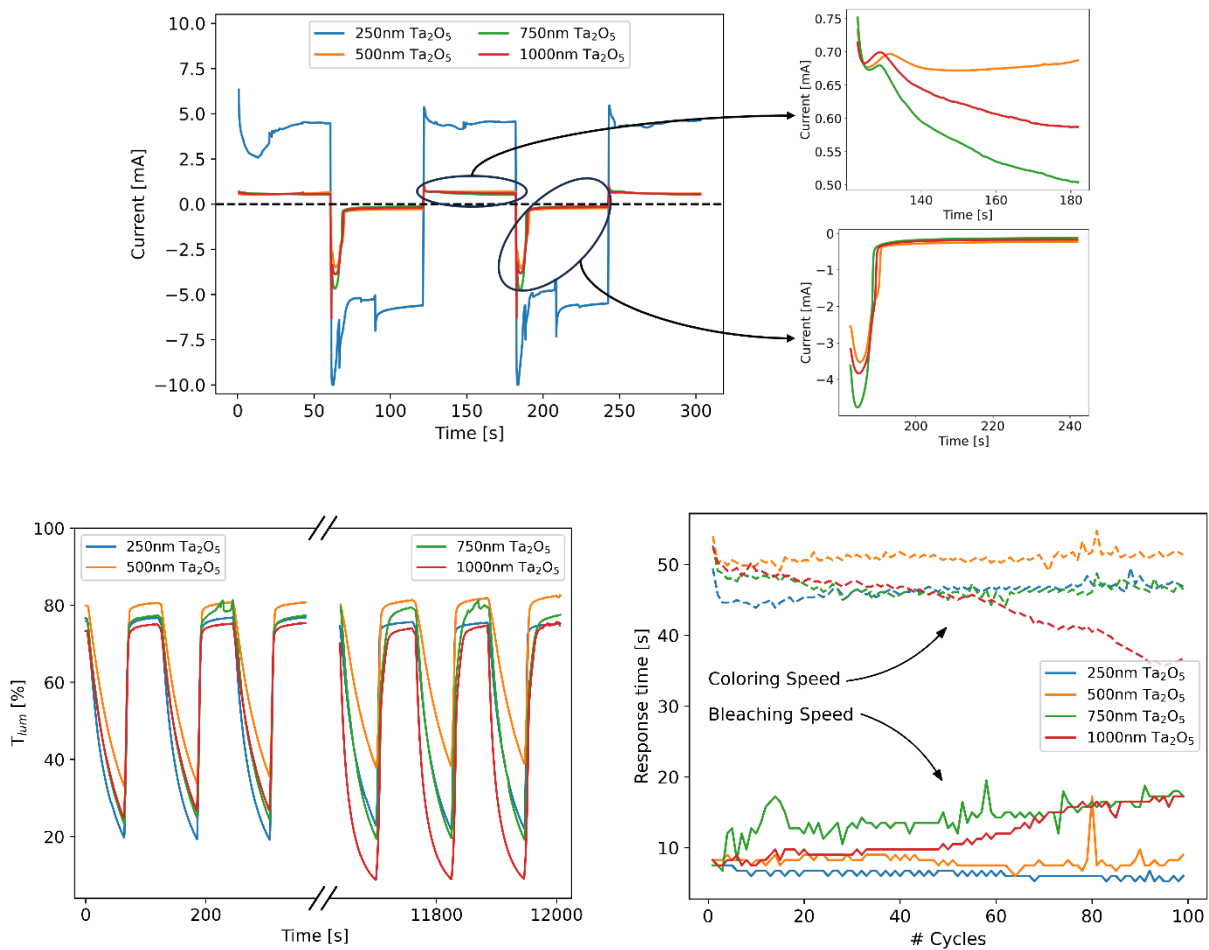


Figure 5.1: Comparison over 100 cycles of (top) the current with a focus on the first coloration and bleaching cycles, (bottom left) the T_{lum} , and (bottom right) the response time needed to reach 90% of the transmission modulation for ASSDs with a 250 nm, 500 nm, 750 nm and 1000 nm Ta₂O₅ layer.

The first main observation here is the presence of a residual current during both the bleaching and coloration processes in ASSDs with the thinner Ta₂O₅ layers (see the top figure in Figure 5.1).

Tang *et al.* suggested that applying a voltage near the breakdown voltage of the oxide materials causes them to lose their insulator behavior, hence leading to an increase in current over time [112]. In addition, they attributed the residual current to defects in the films, resulting in charge leakage through the EC device. As a consequence, the smaller residual currents observed for the ASSDs with the 500 nm, 750 nm and 1000 nm Ta₂O₅ layers demonstrate that increasing the ion conductor thickness helps to reduce the short circuit issue.

The analysis of the luminous transmission in Figure 5.1 (bottom-left figure) reveals interesting findings regarding the impact of the Ta₂O₅ layer thickness on the optical performance of the ASSD. The device with a thicker (1000 nm) Ta₂O₅ layer demonstrates a more efficient coloration process, as evidenced by a significant 14.0% increase in luminous transmission modulation between the first and last cycles. Similarly, the device with a 750 nm Ta₂O₅ layer also benefits from a 4.7% higher ΔT_{lum} after 100 cycles. On the other hand, the devices with 250 nm and 500 nm thick Ta₂O₅ layers exhibit a slight degradation of their colored state, resulting in a decrease in their luminous transmission modulation of 3.6% and 1.1%, respectively. Additionally, the 500 nm Ta₂O₅ ASSD shows a significantly smaller ΔT_{lum} during the overall experiment compared to the other samples. The exact reason for this observation is not clear but may be attributed to the fabrication process of the device.

Regarding the response time of the devices in Figure 5.1 (bottom-right figure), the one with 1000 nm Ta₂O₅ layer demonstrates a notable decrease in its coloration time over time, which comes at the expense of the bleaching time. In contrast, the response time of the other ASSDs remains quite stable after 100 cycles. It is worth noting that the bleaching time for all samples is significantly lower than the coloration time, in agreement with the theoretical expectations (see Section 2.2.1). These results show a promising performance when compared to the literature for EC ASSDs based on the same structure. For instance, Che *et al.* reported a coloration time of 50 s, and a bleaching time of 20 s for a transmission modulation of 39% [50]. However, there is still room for improvement as more efficient devices have been reported in the literature, such as Pan *et al.* who developed an ASSD exhibiting a large transmission modulation of 71% with a coloring and bleaching times of 13 s and 2 s, respectively [113]. These rapid responses could be attributed to the increased porosity of the WO₃ layer, deposited under 30 mTorr, in comparison to 10 mTorr in this work.

After completing the 100 cycles, *in situ* transmission measurements were conducted with an OCP to characterize the loss in transmission over time. The sample with the 250 nm Ta₂O₅ layer exhibited important self-bleaching with a loss of 20% of its transmission after only 5 minutes, whereas the other ASSDs lost less than 5% during the same period. Among the samples, the ASSD with the 750 nm Ta₂O₅ layer showed the highest stability over time, without any obvious self-bleaching. This device configuration led to a $\Delta T_{lum} = 54\%$, which remained consistently stable during the measurements. Subsequent ASSDs were thus fabricated with a 750-nm-thick Ta₂O₅ layer.

5.3 Assessment of the reflection modulation

5.3.1 Limits of the standard ASSD's reflection modulation

WO₃ and NiO are known for their high absorption behavior in their colored state. Thus, the reflection is not expected to exhibit a large modulation and might even decrease upon coloration [8]. However, one of the main objectives of this project was to fabricate an EC ASSD transitioning from a transparent and anti-reflective (AR) state ($R_{lum} < 2.5\%$) towards an opaque and mirror-like behavior ($R_{lum} > 2.5\%$). The AR state can be easily achieved by adding a layer of SiO₂ on top of the device. Therefore, to investigate the best performance in terms of reflection modulation of an ASSD, the homemade Python script described in Section 3.6 was used. Two configurations were considered: the “*standard*” ASSD based on the structure presented in Section 4.3.2, and the “*inverted*” ASSD which consists in inverting the position of the EC materials in the architecture. For each design, the best overall solution out of 86,400,000 possible layer thickness combinations was found based on the chosen figure of merit $\Delta R_{lum}/(R_{lum_B})^3$ and was then reproduced in *Essential Macleod* to model the optical response in terms of reflection, transmission, and absorption, as shown in Figure 5.2. These results are based on the following modeled architectures: Glass substrate / ITO (30 nm) / **WO₃** (329 nm) / Ta₂O₅ (530 nm) / **NiO** (302 nm) / ITO (83 nm) / SiO₂ (72 nm) for the standard design and Glass substrate / ITO (30 nm) / **NiO** (194 nm) / Ta₂O₅ (530 nm) / **WO₃** (260 nm) / ITO (79 nm) / SiO₂ (88 nm) for the inverted structure.

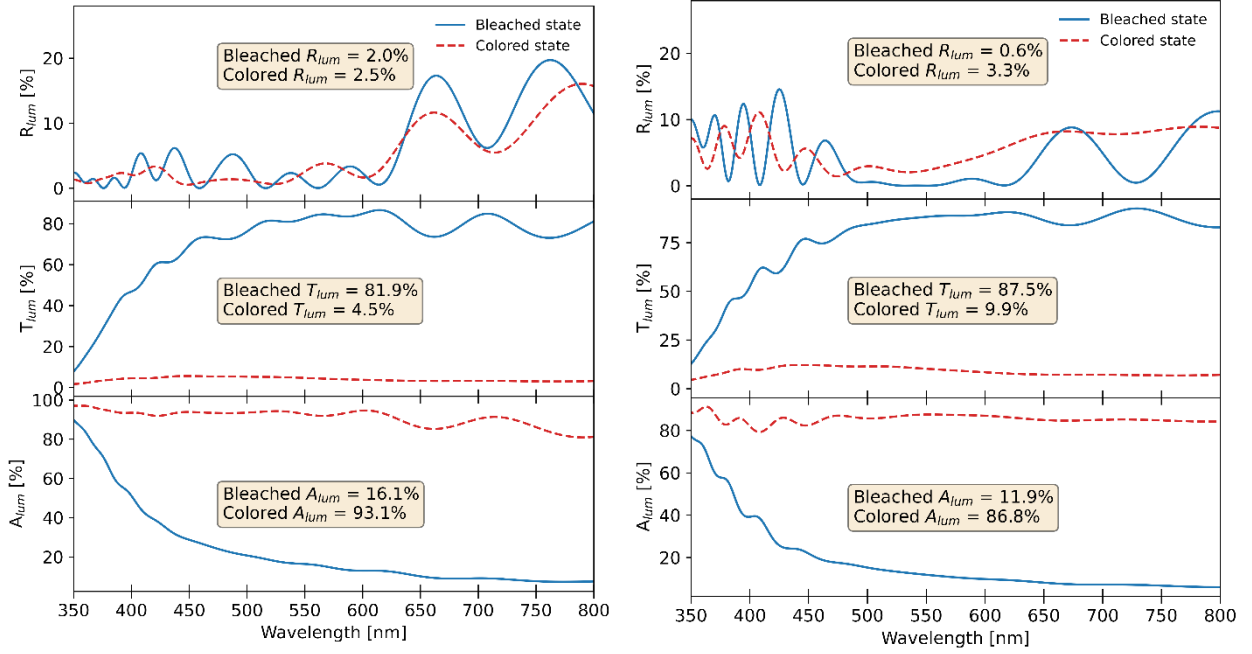


Figure 5.2: Optical response of (left) a standard ASSD and (right) an inverted ASSD, which were optimized to minimize the bleached state reflection while having the highest reflection modulation upon coloration.

Both ASSDs provide excellent transmission and absorption modulations while displaying significant transparency in their bleached state. However, as expected, the standard ASSD's reflection shows a minimal variation with a slight increase of 0.5% upon coloration, despite exhibiting an AR behavior in its bleached state ($R_{lum_B} = 2.0\%$). On the other hand, the inverted structure exhibits a significantly lower luminous reflection in its bleached state ($R_{lum_B} = 0.6\%$), while demonstrating a potential increase of 2.7% upon coloration. This modeling demonstrated that the position of the NiO layer in the ASSD plays an important role as it can impact its optical response. Indeed, because of its higher absorption, the amount of reflected light in the standard ASSD is reduced, thus hindering the desired effect. As a consequence, the inverted structure allowed for a transition from an antireflective bleached state to a mirror-like behavior in the colored state. Nevertheless, it could not achieve the objective of a $\Delta R_{lum} > 10\%$ increase upon coloration.

To investigate the influence of the EC materials' position in the ASSD on its optical response, two devices were fabricated with a standard and inverted structure, considering all thicknesses to be similar. The experimental results are presented in Figure 5.3, showing the chronoamperometry and T_{lum} evolution over time for these two ASSDs. Both devices underwent twenty cycles of ± 3 V potential application, each for 60 seconds. Note that the coloration process was initiated by reversing the polarity of the voltage: + 3V and - 3 V were applied to the standard and inverted ASSDs, respectively. Consequently, during coloration, the standard design displayed positive currents, while the inverted design exhibited negative currents.

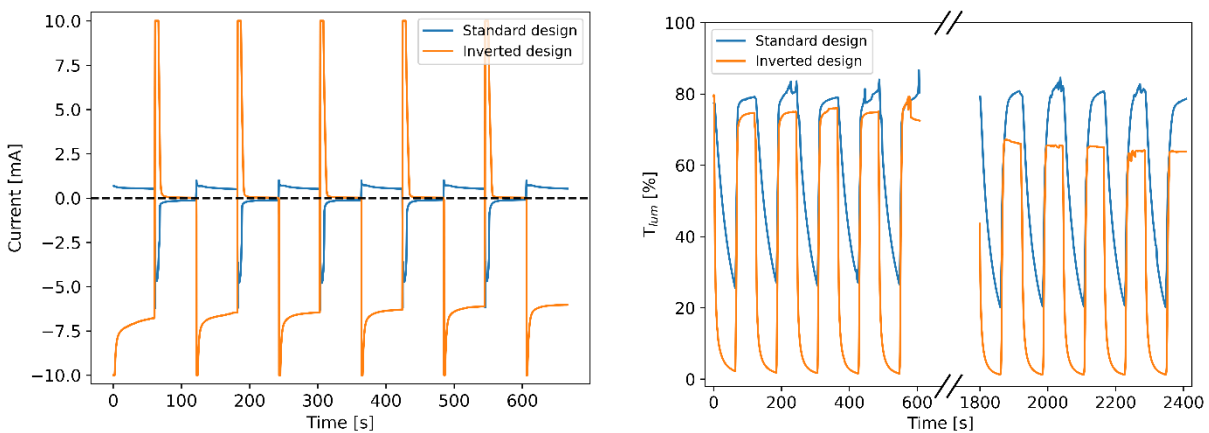


Figure 5.3: (Left) chronoamperometry, and (right) T_{lum} over time for comparison between the standard and inverted designs of ASSD.

The inverted structure exhibits important residual currents during coloration while the bleaching current is lower than the standard device and quickly tends to zero. When analyzing the luminous transmission, the inverted structure demonstrates a significantly higher modulation ($\Delta T_{lum} = 68.4\%$) compared to the standard ASSD ($\Delta T_{lum} = 49.2\%$) during the initial cycles. However, the bleached state of the inverted ASSD is not stable over time, showing a decrease in T_{lum} from 70.9% to 60.6% after the experiment. On the other hand, the colored state is much more intense than the standard architecture which appears to be stable in both states over time. These differences in luminous transmission could be attributed to the upper EC material being closer to the air potentially benefiting from ambient humidity. Therefore, the standard design may have more

protons from water molecules present in the NiO layer, resulting in a more bleached layer. In contrast, the inverted ASSD's WO_3 layer could be more intercalated, becoming increasingly colored over time, affecting both colored and bleached states. In addition, while the ASSDs exhibit a similar bleaching time (7.5 s for the inverted ASSD and 8.3 s for the standard one), they demonstrate significant differences in coloration times.

The inverted structure requires only 15.5s compared to the standard device, which requires 53.4 s. The higher roughness of the NiO layer in the inverted design could be a contributing factor, leading to a less smooth interface with the Ta_2O_5 layer and promoting higher-level porosity in subsequent films. In addition, plasma treatment of the WO_3 layer's surface was performed before the deposition of the top ITO in the inverted ASSD to achieve a smoother interface. However, its impact on the electrode's resistivity was not extensively studied. This could also affect the ASSD performance, as Wang *et al.* [114] demonstrated a higher sheet resistance of the ITO layer deposited on WO_3 compared to the deposition on NiO, resulting in significantly lower kinetics. This has to be considered as in Figure 5.3, the inverted ASSD seems to reach a plateau in T_{lum} for its colored state, while the standard device may achieve lower T_{lum} with a longer voltage application.

5.3.2 A new avenue to promote the reflection modulation

Based on the previous observations, new avenues need to be investigated to provide a transition from an AR to mirror-like state with a reflection increase of 10% (cf. Sub-objective #3). While the literature abounds with examples of electrochromic devices presenting large variations in transmission, a limited number of them address the reflection itself and even less so changes in reflection upon coloration. To this end, quarter-wave optical filters based on periodic Bragg structures can be used as they display an intense and selective reflection peak. The reflection intensity, spectral selectivity, and spectral peak position can be adjusted by refining the structures (bilayer thickness, number of bilayers, index contrast, etc.). Several studies were performed on combining these interference-based structures with EC materials [78, 115, 116]. They aimed at obtaining the highest enhanced reflection in the bleached state, meaning that upon coloration, the increase in the absorption hinders the interference enhancement, thus decreasing the reflectance.

However, fairly recently, Heo *et al.* [9] proposed a new concept implementing alternating WO₃ and ITO layers, both based on colloidal synthesized doped semiconductor nanocrystals, as a quarter-wave optical filter (Bragg mirror). The use of ITO is important as it allows for a better diffusion of electrons by preserving the electronic conductivity throughout the stack. Both materials need to possess a similar refractive index in the bleached state while exhibiting a refractive index contrast upon coloration. WO₃ shows a drop in its refractive index while ITO does not change – generating an optical filter with alternating high and low index layers – resulting in an increase of the reflection upon coloration.

In this work, a similar approach was investigated based on this concept to reproduce WO₃/ITO stacks by magnetron sputtering instead of spin-coating, and integrate these EC Bragg mirrors into an ASSD. The deposition conditions for the ITO in the Bragg mirrors were adjusted so that the refractive index was similar to that of the bleached WO₃ and as a result, minimized its impact on the optical response of the ASSD. Consequently, it is important to distinguish the use of two different ITO films. First, the “*dense*” top ITO layer serves as the transparent electrode (as studied in the previous chapter), which was optimized to limit short circuits and maximize its conductivity. And then, the “*porous*” ITO (same deposition conditions as the dense ITO but with a working pressure of 10 mTorr) in the EC Bragg mirror which was optimized to be porous enough to facilitate ionic diffusion to allow for the coloration of all WO₃ layers, while also being sufficiently conductive. The refractive indices for the porous ITO and the WO₃ in its bleached and most colored states are summarized in Table 5-1.

Table 5-1: Refractive indices at 550 nm of the materials in the EC Bragg filters.

Material	Refractive index at 550 nm
Porous ITO	1.98
Bleached WO ₃	1.92
Colored WO ₃	1.65

As expected, the index contrast between the two materials increases and is of 0.33 upon coloration. While Heo *et al.* [9] obtained a larger index contrast of ~ 0.5 , their films were based on colloidal synthesized nanocrystals which provide higher overall porosity and surface area to volume ratios known to increase the electrochromic activity [115]. However, while it is still possible to achieve a higher contrast with PVD films at the expense of the mechanical durability of the coatings, this is not desired for the current ASSD application. These refractive indices are then used to determine the quarter-wave thickness of the ITO and the colored WO_3 :

$$d = (2m + 1) \frac{\lambda}{4n}, \quad \forall m \in \mathbb{N} \quad (5.1)$$

Here, d and n are respectively the thickness and the refractive index of the layer, and λ is the reference wavelength. The reference wavelength used for the following results is 550 nm as it is the wavelength at which the human eye is the most sensitive. Prior to the implementation in an ASSD, the ITO films' impact on the diffusion coefficient of hydrogen ions was tested by CV by depositing a layer of the porous ITO above a WO_3 film. The addition of the ITO had a minimal impact on the electrochromic performance of the WO_3 (see Figure B.1 in the Appendix). Figure 5.4 presents the modeled reflection response of a 3-bilayer WO_3/ITO stack with an increase of $\Delta R_{lum} = 11.4\%$ upon coloration. It was assumed, for modeling purposes, that each WO_3 layer was equally and fully intercalated. Note that a layer of Ta_2O_5 was added on top in order to finish the stack with a high refractive index to favor the reflection modulation. Its thickness was chosen from Eq. (5.1) with $m = 2$ to allow for a more realistic thickness while minimizing the presence of optical fringes.

Material	Thickness (nm)
Ta ₂ O ₅	326
WO ₃	83
Porous ITO	70
WO ₃	83
Porous ITO	70
WO ₃	83
Porous ITO	70
WO ₃	83
ITO (Delta)	30
Glass substrate	-

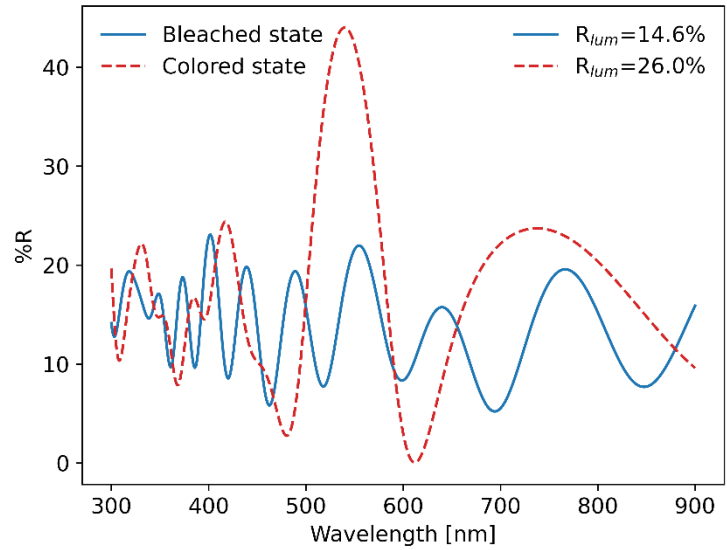


Figure 5.4: Example of (left) the architecture of a 3-bilayer WO₃/ITO stack, and (right) the resulting peak in reflection at 550 nm upon coloration.

In addition, Figure 5.5 illustrates the modeled impact of the number of WO₃/ITO bilayers covered by the Ta₂O₅ layer on the luminous reflection and the luminous transmission.

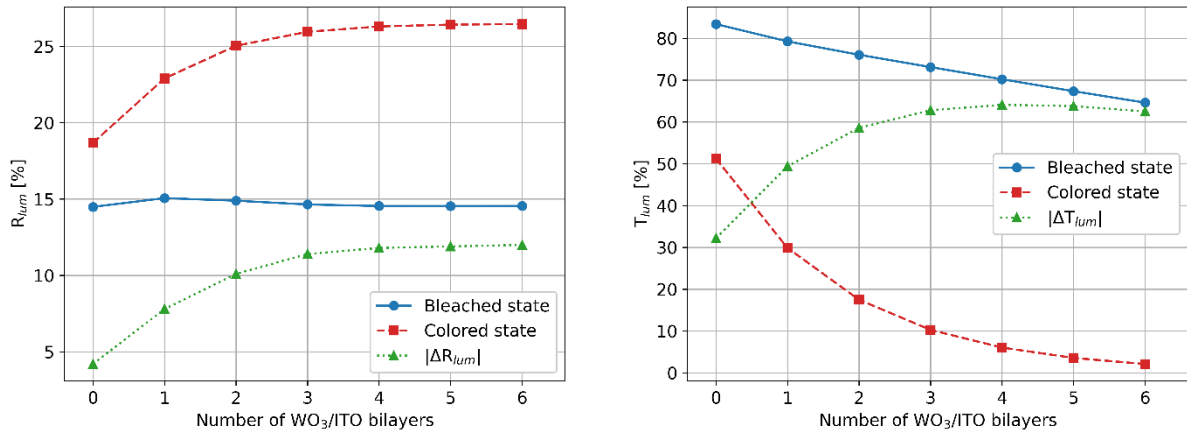


Figure 5.5: Impact of the number of WO₃/ITO bilayers on the luminous reflection and the luminous transmission.

Hence, modeling shows the possibility of an increase greater than 10% from at least 2 bilayers while keeping a sufficient transmission modulation. It is interesting to notice a limitation of the present concept as the ΔR_{lum} saturates around 12% when considering 3 bilayers and more, as well as a drop in the bleached state transmission, which are due to the increasing absorption in the WO_3 . However, to reproduce such an architecture, which represents only half of a complete ASSD, the colored state would need to be obtained by using a chemical intercalation process. Most of the samples tested in this way showed important delamination of the layers or significant charge trapping leading to a non-negligible blue tint in the bleached state. To prevent these issues, these stacks need to be directly implemented into ASSDs by simply replacing the WO_3 layer in the device. Note that the limited refractive index change of NiO at 550 nm ($\Delta n = 0.03$) prevents the use of such EC Bragg mirrors using this material.

5.3.3 Implementation of the EC Bragg mirror in an ASSD to maximize the reflection modulation

This new avenue concerning EC Bragg mirrors incorporated in ASSDs showed promising results (presented below) for Essilor's applications in the eyewear industry. The previously described literature review did not show any practical implementation of such structures. Hence, the novelty of this approach has resulted in a patent application. In this case, a significant amount of time was dedicated to determining the ideal ASSD structure to provide the transition from an AR to mirror-like behavior. Therefore, modeling with the brute force approach and *Essential Macleod* were once again used. Different configurations were investigated, as illustrated in Figure 5.6 to highlight the benefits of incorporating the EC Bragg mirrors in an ASSD for both the R_{lum_B} and ΔR_{lum} . Both the standard and inverted structures were considered here for comparison, as well as the impact on the R_{lum_B} and ΔR_{lum} upon coloration of the SiO_2 layer on top of the devices.

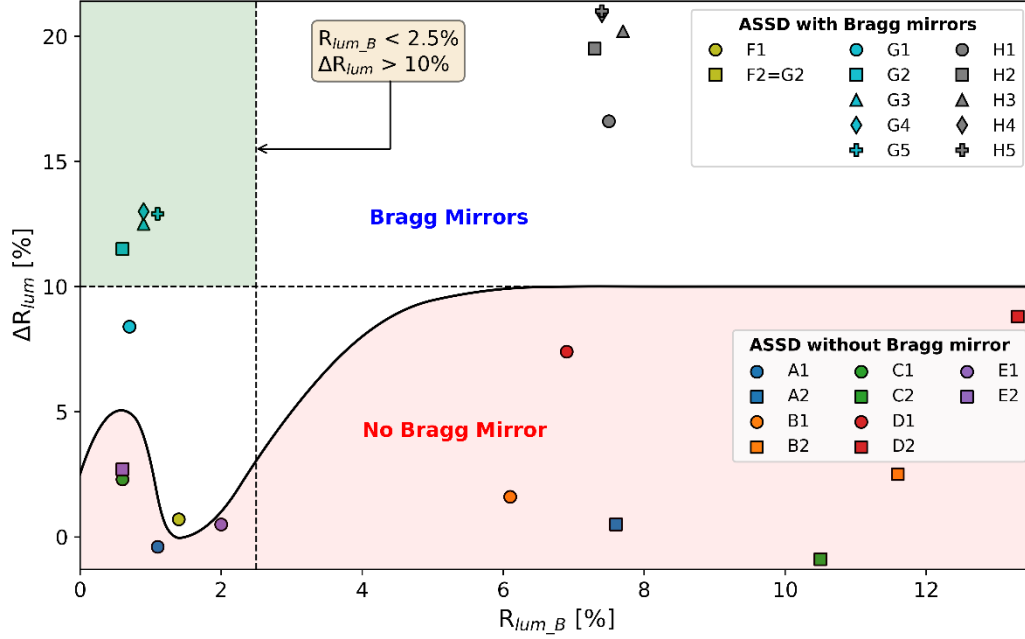


Figure 5.6: Summary of the results comparing R_{lum_B} with ΔR_{lum} for all the modeled designs in Table C-1 (see the Appendix), showing the benefits of implementing the EC Bragg mirrors in an ASSD.

The different labels refer to various structures obtained by modeling (more details about these different designs are given in the Appendix - refer to Table C-1):

- Standard architecture of the ASSD with (**A1**) and without (**A2**) SiO_2 to minimize R_{lum_B} .
- Standard architecture of the ASSD with (**B1**) and without (**B2**) SiO_2 to maximize ΔR_{lum} .
- Inverted architecture of the ASSD with (**C1**) and without (**C2**) SiO_2 to minimize R_{lum_B} .
- Inverted architecture of the ASSD with (**D1**) and without (**D2**) SiO_2 to maximize ΔR_{lum} .
- Standard (**E1**) and inverted (**E2**) architecture of the ASSD with SiO_2 to maximize $\Delta R_{lum}/(R_{lum_B})^3$.
- Incorporation of a 2-bilayers WO_3/ITO stack in a standard (**F1**) and inverted (**F2**) architecture of the ASSD with SiO_2 to minimize R_{lum_B} .

- Implementation of *i*-bilayers WO₃/ITO stack (**Gi**) in an inverted architecture of the ASSD with SiO₂ to minimize R_{lum_B} .
- Implementation of *i*-bilayers WO₃/ITO stack (**Hi**) in an inverted architecture of the ASSD with SiO₂ to maximize ΔR_{lum} .

When considering the designs without the EC Bragg mirrors, Figure 5.6 demonstrates that the top SiO₂ is crucial to achieving an AR ASSD in the bleached state (see **A1** vs **A2** and **C1** vs **C2**). On the other hand, removing the constraints on the bleached state reflectance allows for a slightly higher ΔR_{lum} (see **B1** vs **B2** and **D1** vs **D2**). It also supports the observations in Section 5.3.1 when comparing the standard (**E1**) and inverted (**E2**) designs as the latter exhibits lower R_{lum_B} and higher ΔR_{lum} even when compared to the implementation of the Bragg mirrors in the standard ASSD (**F1**). Finally, it can be clearly observed that the only means by which one can reach the desired green region, where R_{lum_B} is below 2.5% and ΔR_{lum} is above 10%, is by the insertion of ITO quarter-wave layers in an inverted design of an ASSD (**Gi designs**). Once again, it is possible to achieve significantly higher ΔR_{lum} if minimizing the R_{lum_B} is not crucial (**Hi designs**).

Specifically, we focused on the designs **Gi** from Figure 5.6 to determine the impact of the number of bilayers in the ASSD on the reflection and transmission, as presented in Figure 5.7.

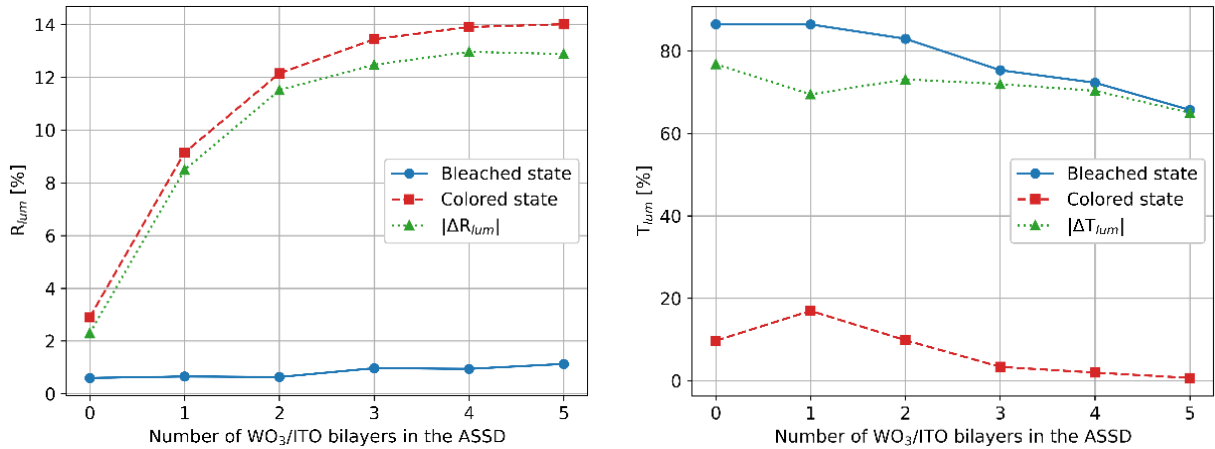


Figure 5.7: Evolution of (left) R_{lum} and (right) T_{lum} depending on the number of bilayers in the inverted ASSD.

The objective of obtaining a $\Delta R_{lum} > 10\%$ while being AR in the bleached state is possible from at least a 2-bilayer WO_3/ITO stack in the inverted ASSD. The above results show a saturation in the R_{lum} modulation of around 13% upon the increase of the number of bilayers in the ASSD as the presence of absorption in the WO_3 starts to limit the interference-enhanced-reflection. However, considering that the AR ASSD without the EC Bragg mirrors could only achieve a 2.3% increase in reflection while being AR, and that only one bilayer leads to a 8.5% increase, the present EC Bragg mirror solution is, indeed, very efficient.

This represents a significant milestone in the context of the present project as previous work performed at the FCSEL demonstrated the difficulty to produce such functional devices with an important reflection modulation [8]. Furthermore, increasing the number of bilayers also impacts the transmission in the colored state which gets lower the higher the number of bilayers, because of the increase in the overall thicknesses of the EC materials present in the ASSD. Therefore, for ASSDs implemented in ophthalmic applications, the choice of a lower number of bilayers would seem to be more adequate as it facilitates the fabrication of such devices and minimizes the possible issues due to the increase in the number of interfaces in the device. Indeed, Baloukas *et al.* demonstrated that the increase of interfaces with layers possessing different ionic diffusion coefficients [78] and different electronic conductivities [115] seems to favor the presence of charge trapping. Hence, an inverted device with 2-bilayers was fabricated, while monitoring the deposition thicknesses by *in situ* ellipsometry measurements, in order to obtain a performance as close to the modeling as possible. The ASSD's reflection was also measured before and after the deposition of an 88 nm SiO_2 layer to observe the impact of the AR layer on the bleached state reflection (Figure 5.8).

Material	Thickness (nm)
SiO ₂	88
Dense ITO	95
WO ₃	83
Porous ITO	70
WO ₃	83
Porous ITO	70
WO ₃	83
Ta ₂ O ₅	535
NiO	200
ITO (Delta)	30
Glass substrate	-

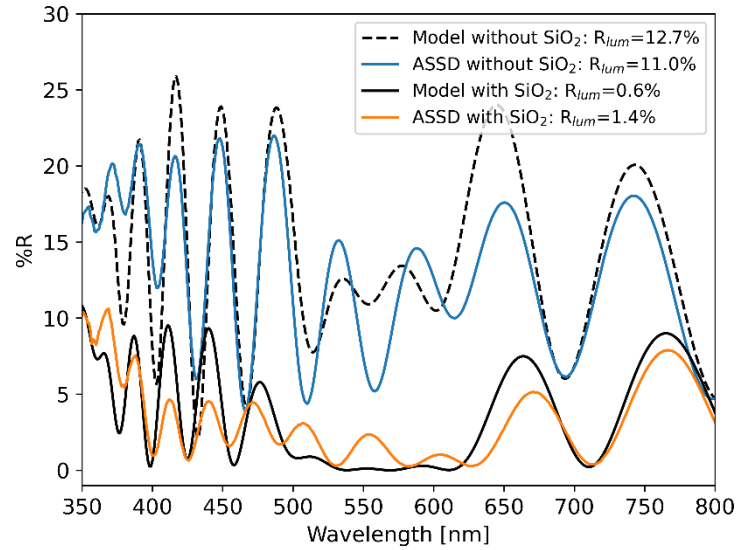


Figure 5.8: (Left) architecture of an ASSD with a 2-bilayer WO₃/ITO stack and (right) impact of an 88 nm SiO₂ layer on its bleached state reflection and comparison with modeling.

As expected, the ASSD's reflection is significantly reduced after the SiO₂ deposition, decreasing the R_{lum} by approximately 10% and an AR behavior is indeed achieved ($R_{lum} = 1.4\%$), despite showing a discrepancy with the modeled performance. This difference can be due to the fact that the charges are not uniformly distributed within the device. It can also be related to a loss of charges in the ASSD over time considering the small size of the hydrogen ions [117]. Hence, the measured "bleached" state could be altered as the NiO is unable to reach its most transparent state during the characterizing phase (see Section 4.2.3). Finally, the NiO's different bleached and colored states were characterized in a KOH solution, resulting in the use of OH⁻ ions during intercalation, which could present some discrepancies with the present layer that is deposited under vacuum with H⁺ ions [10]. Nevertheless, this ASSD's reflection modulation was characterized over 20 cycles of alternating +/- 3V for 1 minute each and finally for 3 minutes to try to reach the highest reflection

modulation possible as shown in Figure 5.9. The figure also exhibits the reflection spectra in the bleached and colored state of the AR ASSD to compare the experimental results with modeling.

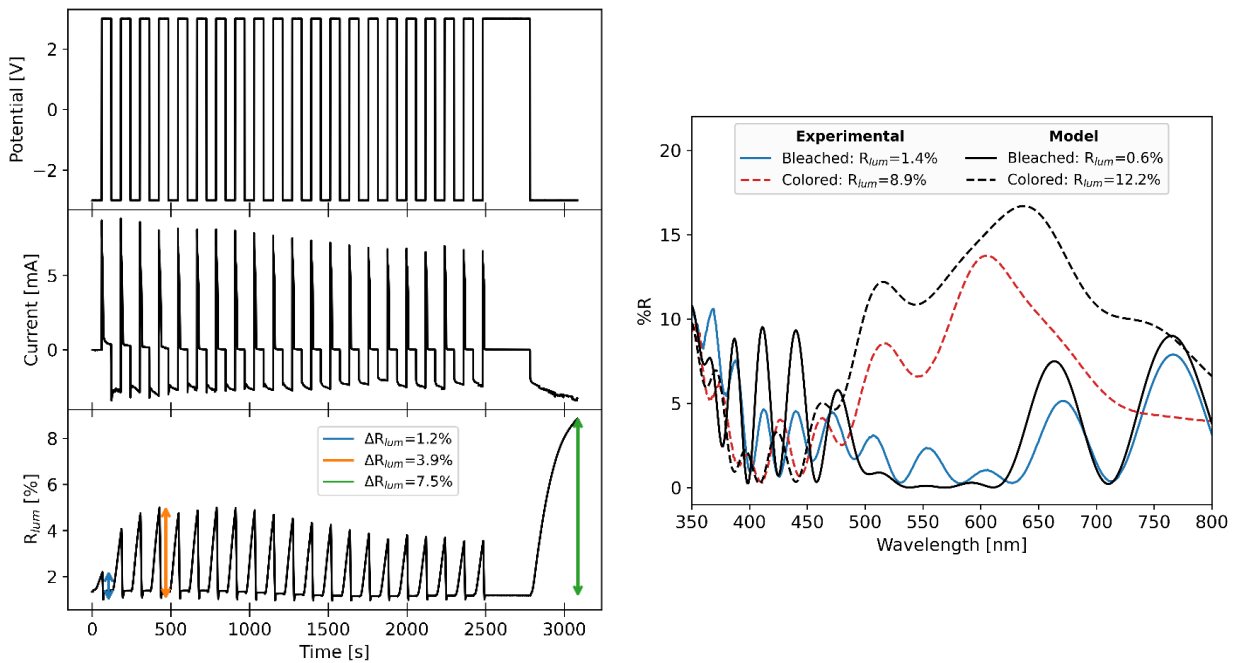


Figure 5.9: (Left) evolution of the potential, current and R_{lum} over time and (right) comparison between modeling and experimental reflection spectra for the ASSD containing a 2-bilayer WO_3/ITO stack.

The left figure shows a relatively low reflection modulation for the first two cycles ($\Delta R_{lum} = 1.2\%$) during the activation phase, while it reaches a maximum of 3.9% after the third cycle. At the end of the 20 cycles, a longer application of the potential led to an increase of $\Delta R_{lum} = 7.5\%$ from an AR bleached state. Two previous samples based on the same design were also analyzed after deposition without *in situ* monitoring. However, only the last sample for which the results are shown here, was able to reach a fully transparent state after the 3 minutes of bleaching. While the first two samples achieved a significant reflection modulation of $\Delta R_{lum} = 7.0\%$ during the longer coloration phase, they were not AR from the start and presented a residual brownish color after bleaching. This may be related to a non-sufficient number of charges to fully bleach the NiO .

Further studies are required to fully understand the reason why these samples showed such a difference in performance.

Finally, an important aspect shown in the right figure is the difference between the bleached and colored states. A reflection peak is obtained upon coloration in the 500 nm to 700 nm range even though the sample is antireflective in its bleach state. Yet, the significant breakthrough achieved in this study is the remarkable luminous reflection modulation, which is nearly three times higher than that of an inverted ASSD without the EC Bragg mirror (7.5% compared to 2.7% obtained through modeling in Section 5.3.1). However, it is obvious, here, that the reflection modulation is lower than what is expected by the model, and the shape of the colored state, while following a similar trend, does not fit well the modeled curve. To explore the potential reasons behind the observed differences, additional modeling studies were performed. One important hypothesis that was made earlier, is that all of the WO_3 layers in the WO_3/ITO stack reach their most colored state. Figure 5.10 highlights the impact of reducing the coloration levels reached by the WO_3 in the ASSD (using the optical properties obtained by coloring the WO_3 at different voltages, see Section 4.2.3) while still maintaining the same intercalation level in all the WO_3 layers.

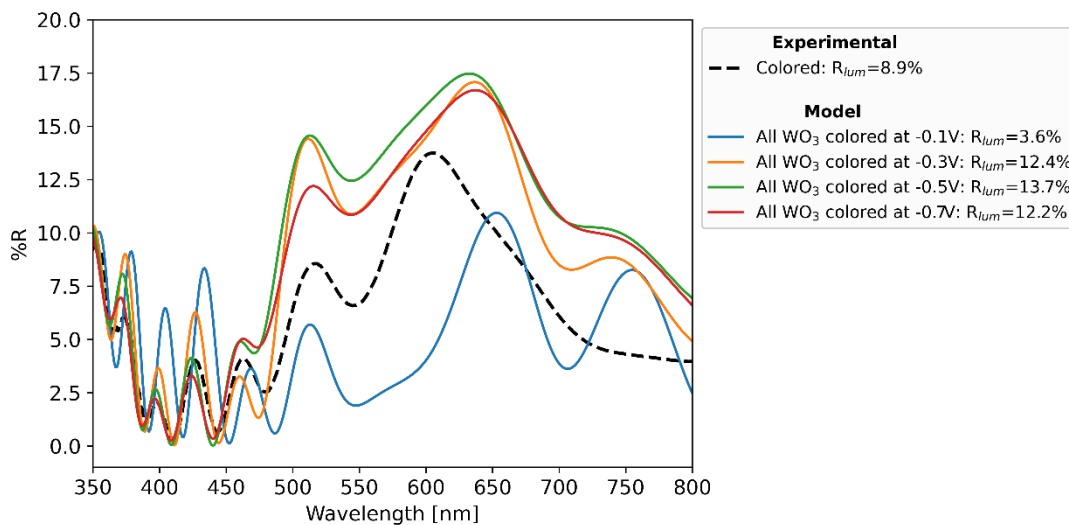


Figure 5.10: Modeled reflection for different coloration levels of the WO_3 layers in the ASSD.

It is observed that no curve seems to fit with the experimental results, showing that more work needs to be done to fully understand the coloration mechanism of the WO_3 layer. Nevertheless, the

experimental curve seems to be in between the ASSD with all WO_3 layers colored at -0.1 V and -0.3 V. Hence, more intermediate coloration states should be characterized to obtain a more precise panel of optical responses of such ASSDs. It can also be observed that the model indicates an overall higher performance at a lower intercalation (-0.5 V) whereas the transmission continues to decrease upon coloration, and thus the absorption increases. However, this phenomenon did not appear in the *in situ* measurements, suggesting that the WO_3 layers may not reach their highest coloration level in the present case. A final analysis is performed to question the hypothesis of all WO_3 layers being colored at the same intercalation level. Hence, Figure 5.11 shows the reflection response when the EC layers in the Bragg mirror are colored at different levels to get closer to the measured reflection experimentally, where the WO_3 closest to the Ta_2O_5 is supposed to possess a higher intercalation ratio.

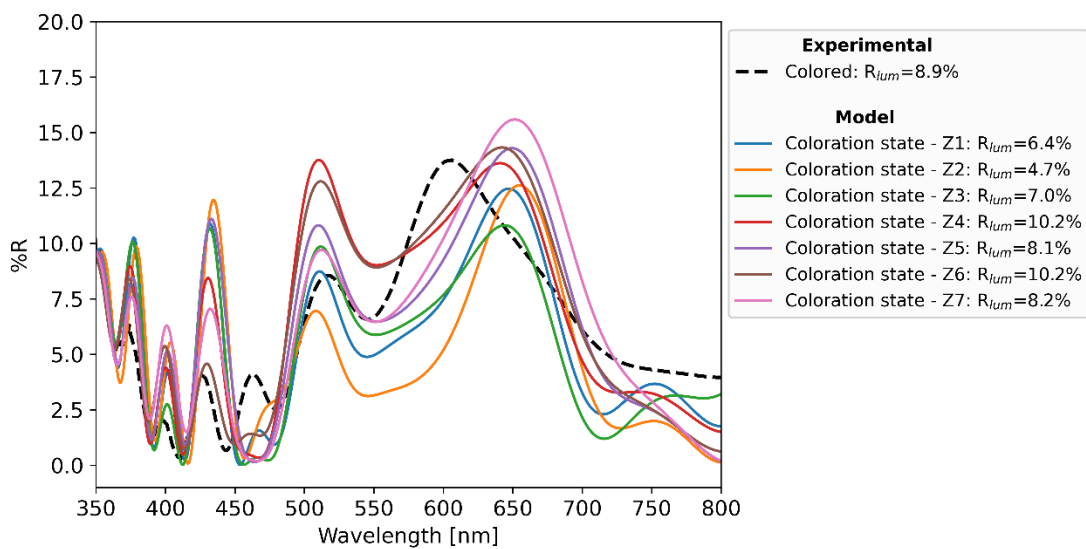


Figure 5.11: Modeled reflection with the WO_3 layers in the Bragg mirror incorporated in an ASSD colored at different intercalation levels. More details are given in Table 5-2.

While no model curve from Figure 5.11 explicitly fits the experimental data, they do seem much closer to the experimentally obtained results. This highlights the limitations of assuming that all of the WO_3 layers are colored at the same intercalation level during modeling. Therefore, these results indicate that the first layer closest to the Ta_2O_5 would be fully colored whereas the second and third

layers would reach lower intercalation levels. Once again, this could result from the difference in the ionic diffusion and electronic conductivity between the WO_3 and porous ITO layers, which hinder the ionic diffusion process through the overall Bragg mirror.

Table 5-2: Details of the structures **Zi** from Figure 5.11, describing the coloration levels of the different WO_3 layers. It was supposed that the WO_3 layers closest to the Ta_2O_5 layer are expected to exhibit a greater degree of intercalation.

	Coloration levels of the WO_3 in the Bragg structure incorporated in an ASSD
Z1	... Ta_2O_5 / WO_3 (-0.3 V) /porous ITO/ WO_3 (-0.1 V) /porous ITO/ WO_3 (-0.1 V) / dense ITO
Z2	... Ta_2O_5 / WO_3 (-0.3V) /porous ITO/ WO_3 (-0.1V) /porous ITO/ WO_3 (B) / dense ITO
Z3	... Ta_2O_5 / WO_3 (-0.7V) /porous ITO/ WO_3 (-0.1V) /porous ITO/ WO_3 (-0.1V) / dense ITO
Z4	... Ta_2O_5 / WO_3 (-0.7V) /porous ITO/ WO_3 (-0.3V) /porous ITO/ WO_3 (-0.1V) / dense ITO
Z5	... Ta_2O_5 / WO_3 (-0.7V) /porous ITO/ WO_3 (-0.3V) /porous ITO/ WO_3 (B) / dense ITO
Z6	... Ta_2O_5 / WO_3 (-0.7V) /porous ITO/ WO_3 (-0.7V) /porous ITO/ WO_3 (-0.1V) / dense ITO
Z7	... Ta_2O_5 / WO_3 (-0.7V) /porous ITO/ WO_3 (-0.7V) /porous ITO/ WO_3 (B) / dense ITO

It is worth mentioning that an ASSD with a 1-bilayer WO_3 /ITO stack and no SiO_2 layer on top was fabricated. The idea was to explore the increase in reflection while removing the constraints on the AR bleached state. The results are shown in the Appendix (Figure D.1) and demonstrate a significant increase of $\Delta R_{lum} = 11.7\%$. Hence, the targeted 10% increase was achieved, although not from an AR state as specified in Section 1.3.

5.3.4 Enhancing the concept of EC Bragg mirrors in an ASSD

As shown previously, the implementation of EC Bragg mirrors in an ASSD often leads to charge trapping, hence some devices were unable to reach a fully transparent state after only a few cycles.

It is noticeable that a similar behavior was also observed by Heo *et al.* [9]. As mentioned earlier, this can be explained by the difference in ionic or electron diffusion coefficients at the layers' interface, which can lead to disruptions in the charge displacement and also hinder the hydrogen ions' diffusion through all WO₃ layers. However, considering that the issues encountered were not observed during coloration, but only during the bleaching of the ASSDs, the electron diffusion may be the main cause of this charge trapping. The porous ITO could be deposited at higher pressures to obtain a more porous, but less conductive, layer which could enhance the flow of ions through all the layers of WO₃ in the EC Bragg mirror. The conductivity of the porous ITO can also be easily altered by introducing oxygen during the deposition while maintaining a minimum amount of conductivity to allow for the transfer of electrons through the layers, a prerequisite for the coloration process. Hence, a sample was prepared by adding 5% O₂ vs Ar concentration to the previous deposition conditions for the porous ITO to increase its overall resistivity (from $3.1 \times 10^{-5} \Omega.m$ to $9.8 \times 10^{-5} \Omega.m$). A 2-bilayer WO₃/ITO stack ASSD without a top SiO₂ was then deposited aiming at obtaining a maximum reflection modulation while omitting the AR constraint. The obtained results are shown in Figure 5.12, based on a non-AR ASSD containing a 2-bilayer WO₃/ITO stack with the following thicknesses: ITO Delta (30 nm), NiO (196 nm), Ta₂O₅ (552 nm), porous ITO (68 nm), WO₃ (83 nm) and dense ITO (86 nm).

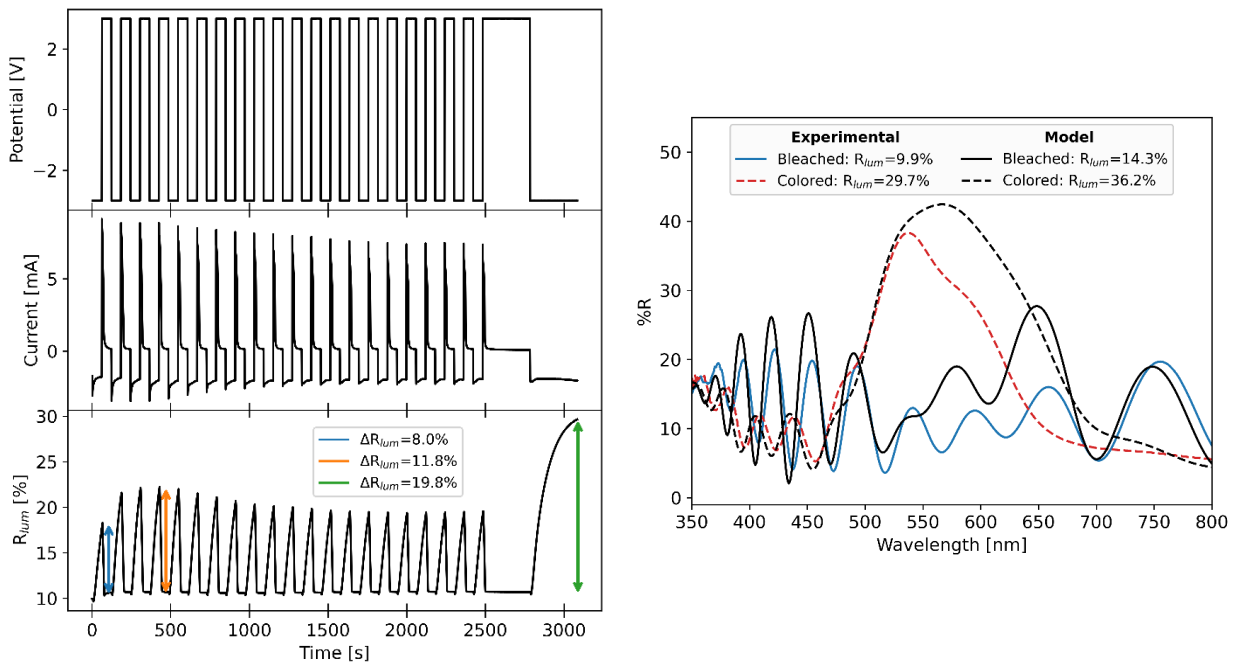


Figure 5.12: Results for the ASSD with the 2-bilayers of WO_3/ITO with the altered ITO conductivity.

These figures illustrate an important reflection modulation of up to $\Delta R_{lum} = 19.8\%$ while being able to fully recover its bleach state after the final coloration. While closer to the modeled curves, the experimental spectrum still exhibits discrepancies and is unable to reach as high a luminous reflection as the model from *Essential Macleod*.

It is relevant to mention that the experiment performed here is only an opening for future work on this concept, as the idea was not pushed further. Future work can be done to ensure that the electron diffusion coefficient is similar to that of WO_3 to minimize the presence of space-charge limitation effects at the interfaces [116]. If this avenue is not sufficient to enhance the functionality of EC Bragg mirrors implemented in ASSDs, another solution to avoid interface issues would be to create a gradient between the layers by co-sputtering of the two materials to create a smoother transition such as $\text{WO}_3 \mid \text{WO}_3\text{-ITO} \mid \text{ITO} \mid \text{ITO-WO}_3 \mid \text{WO}_3$. Finally, to enhance the reflection modulation, the deposition conditions can be adjusted to enhance the refractive index contrast between the ITO and the colored WO_3 , which can be obtained by depositing a slightly denser ITO. In this case, a

balance would need to be found to avoid increasing charge trapping between different density layers.

5.4 ASSD durability

When considering the industrialization of ASSDs in ophthalmic lenses, the voltage value and duration required to transition between the bleached and colored states, and *vice-versa*, are important factors. The impact of the voltage application duration is quite forward since the longer the voltage is applied, the deeper the ions are lodged into the EC layers. This increases the probability that the ions will reach deep irreversible trap sites in the microstructure of the material.

An experiment was thus performed to quantify the performance of an inverted ASSD when varying the voltage conditions: ± 1 V, ± 2 V, and ± 3 V, with each voltage applied for 15 seconds over 10 cycles. The results of this experiment are presented in Figure 5.13:

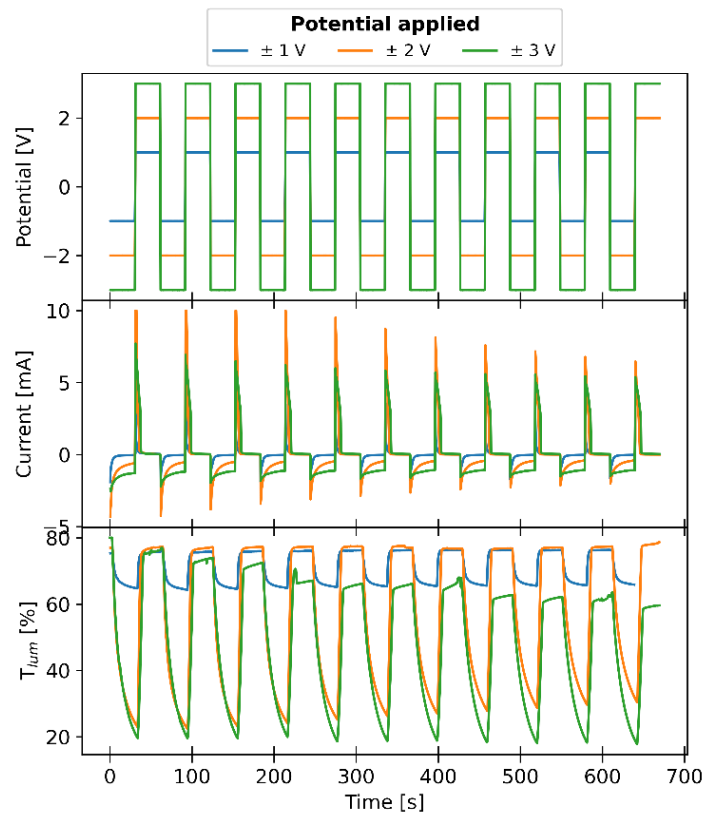


Figure 5.13: Evolution of the potential, current, and T_{lum} over time while varying the potential applied to the ASSD.

It can be seen that applying ± 1 V does not achieve a significant range of transmission modulation, while the use of ± 3 V leads to rapid deterioration of the bleached state over the cycles. Therefore, despite being slightly unstable regarding the colored state, the optimal choice of voltage lies in the application of ± 2 V. These results comply with the existing literature [85, 118].

Finally, a durability test was conducted on an inverted ASSD without the presence of an EC Bragg mirror. It involved the application of ± 2 V for 15 seconds each for 1000 cycles. As mentioned previously, the potential was intentionally reduced to ensure a better life cycle of the device. The result of this experiment is shown in Figure 5.14.

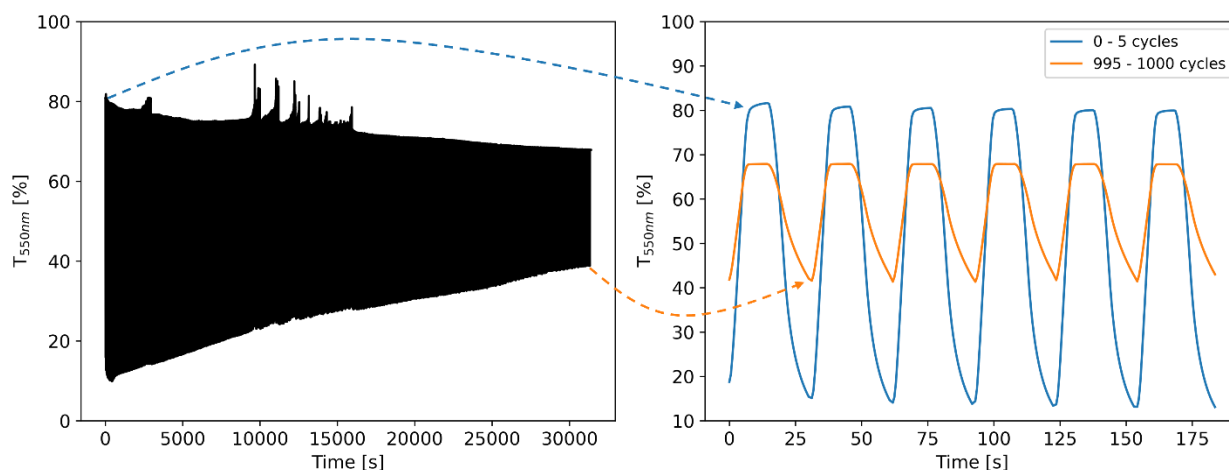


Figure 5.14: Evolution of the transmission at 550 nm over 1000 cycles of ± 2 V applied each 15 seconds.

The durability test reveals a drop in the transmission modulation from 67% to 27% after 1000 cycles, where both the bleached and colored states are affected by the experiment. This has often been observed in the literature [54], and is typically ascribed to charge trapping in reversible sites, shielding the insertion of further ions, thus gradually limiting the coloration of the material. The ions can also be trapped in deep irreversible sites of the WO_3 layer inducing a degradation of the bleach state over time. It appears that the method of applying the potential plays an important role as the high and abrupt application of a voltage may lead to charge accumulation at the interface

and thus increased probability of charge trapping [119]. Further investigations are necessary to explore the optimal approach for the application of the potential, such as applying intermediate potential steps [119], using pulsed high voltages or pulsed currents with buffer times between each pulse [120].

5.5 ASSD fabricated on Essilor's substrates

Thanks to an effective cleaning procedure and fabrication methodology, it was possible to produce multiple functional ASSDs successfully and systematically on an ITO-coated glass substrate. This enabled to investigate the possibility of depositing devices on alternative substrates, such as ophthalmic lenses. However, two significant challenges were encountered: the difficulty to obtain a performance for the bottom ITO on par with the previously used commercial ITO, and the polymer substrate, which is more sensitive to stresses and temperature. To optimize the ITO conductivity on a glass substrate, the material is usually heated at high temperature to activate the Sn dopants. However, this approach becomes impractical when depositing ITO on polymer substrates, which can limit its performance. Consequently, for the bottom ITO layer, the deposition conditions were chosen to be the same as the top dense ITO mentioned earlier. Several ASSDs were fabricated on the ophthalmic lenses, but they all showed the presence of stress in the device due to the ITO cracking during the deposition, leading to a highly non-uniform coloration of the sample. To address the ITO cracking issue, a 200 nm SiO_2 layer was added to the substrate prior to the deposition of the ASSD. This additional layer was supposed to work as a protective barrier to lower substrate deformation. Yet, despite minimizing the presence of cracks, it still resulted in significant non-coloration of the sample, as shown in Figure 5.15:

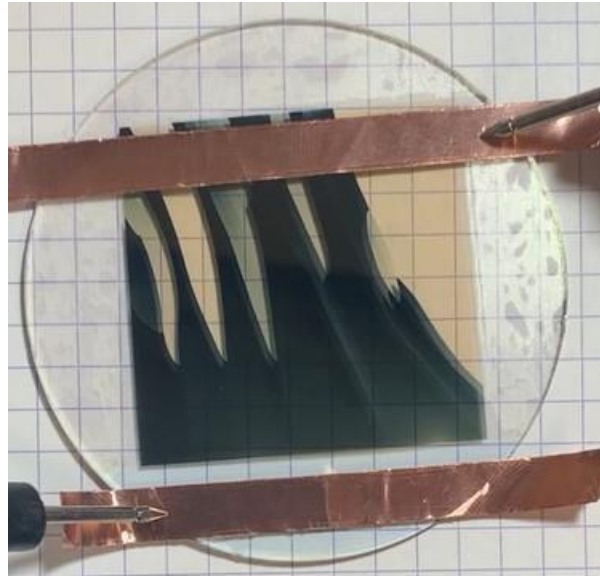


Figure 5.15: Picture of an ASDD fabricated on ophthalmic lenses.

In addition, as the cracks seem to appear quite early during the ASDD deposition due to the thermal expansion of the substrate, having a thinner and more efficient bottom electrode was explored: instead of depositing a 100 nm ITO thin film, a thin more ductile layer of Ag (15 nm) with a thin layer of ITO (30 nm) were used as the bottom electrode to try and improve the functionality of the device. Despite this, the device suffered from similar issues as the ones shown in Figure 5.15. An additional untested approach that can be investigated in the future would be to use a substrate holder with a hole enabling the substrate to be freestanding and unconstrained. This could potentially reduce the amount of stress in the final ASDD.

CHAPTER 6 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

The objective of this project was to produce a fully functional EC ASSD prototype that can transition from a state of high transmission and low reflection to a state of low transmission and high reflection. To achieve this objective, a thorough cleaning methodology was developed and implemented, which proved to be highly effective in reducing the presence of defects and particles on the substrate surface. However, it was observed that the edges of the substrates presented challenges in achieving the desired cleaning efficiency. To address this issue, additional steps were introduced during the fabrication procedure to allow for the successful fabrication of functional ASSDs, ensuring the reliable and systematic production of devices without obvious short circuit occurrences (cf. sub-objective #2 defined in Chapter 1). In addition, the extensive characterization of each ASSD's layer enhanced the overall device EC performance and transmission modulation for eyewear purposes (cf. sub-objective #1 defined in Chapter 1). However, the positions of the anodic and cathodic EC layers appeared to significantly impact the optical response of the ASSD. The development of an inverted device structure demonstrated the transition from an AR behavior in the bleached state to a mirror-like state upon coloration, with a maximum increase from 0.6% to 3.3%.

To achieve the targeted 10% increase in reflection specified in sub-objective #3 defined in Chapter 1, a new approach involving an EC Bragg mirror based on alternating WO_3 and ITO layers in the ASSD was explored. Extensive modeling work garnered significant interest from Essilor, leading to a patent submission¹. Extensive modeling demonstrated that incorporating this new concept in an inverted structure was the only way to achieve a 10% increase in reflection. Although the modeling exhibited a possible 11.6% increase from an AR state upon coloration, the experimental AR ASSDs fabricated with a 2-bilayer WO_3 /ITO stack was only able to increase its reflection by 7.5%, which was still significantly higher than the regular device. When withdrawing the constraint

¹ At the moment of writing this thesis, the patent was under preparation.

on the AR state by removing the SiO₂ layer on top of the ASSD, it was possible to achieve a greater reflection modulation. Indeed, an attempt to improve the durability of the ASSDs with incorporated Bragg mirrors, resulted in an important increase in reflection of $\Delta R_{lum} = 19.8\%$.

The experiments performed regarding the durability of the developed ASSDs highlighted a need for improvement by fully understanding the ion trapping phenomenon that occurred upon extended cycling. This phenomenon is likely to arise from side reactions in the materials, which hinder the efficiency of intercalation and deintercalation in the EC materials. Additionally, the way the potential was applied at the electrodes played a crucial role, as prolonged application of high voltages appeared to increase the probability of charge trapping by creating potential charge accumulations at the interfaces. Finally, experiments were conducted using a polymer substrate commonly employed in ophthalmic lenses. However, it was observed that the introduction of this new substrate had a notable impact on the success of fabricating functional ASSDs as it exhibited the formation of important cracks in the device, which compromised their ability to achieve uniform coloration. Overcoming this challenge is crucial to provide EC ASSDs suitable for curved or flexible substrates for smart eyewear applications. While mechanical tests were not conducted due to time constraints, it is recognized that there are still several avenues for improvement before achieving a fully reliable prototype.

Upon reviewing the project's objectives, it is clear that significant progress has been made, and that many of the defined goals have been achieved. However, there are some valuable recommendations that have emerged throughout the project, particularly regarding the improvement in the WO₃/ITO interfaces for the EC Bragg mirrors and the enhancement of the durability of the ASSDs.

6.2 Recommendations

Throughout this project, the focus was on characterizing the ASSDs during the bleaching and coloring processes, either for their transmission or reflection. However, to gain a more in-depth understanding of their performance during these dynamic processes, a new setup is recommended to enable the simultaneous *in situ* measurement of both optical responses. This would enable to visualize the dependency between transmission and reflection, thus, helping to further optimize

their design and performance for practical applications. Moreover, while the properties of the different materials used in this project were sufficient for the fabrication of functional ASSDs, there is still room for further improvement to enhance their overall performance. For instance, the dense ITO deposition conditions can be refined to achieve better conductivity and transparency, maximizing its effectiveness as a TCE. As depicted in Section 5.3.4, the porous ITO can also be optimized to match with the WO_3 ionic and electronic conductivities. In addition, it would be beneficial to conduct further research on NiO 's and WO_3 's properties to improve the charge balance between these two EC materials, while maintaining the highest possible transmission in the bleached state.

An important consideration in this project is that most of the current research and commercialized EC products use lithiation (Li^+ ions) rather than hydrogenation (H^+ ions) as the intercalated ion. While increasing the size of the intercalated ion could potentially prevent charge loss over time, it may also increase charge trapping within the layers of the ASSDs. Shifting to Li^+ ions would require chemical pre-intercalation in a LiClO_4 -PC electrolyte. It would also result in more reliable devices as it minimizes side reactions with adsorbed water from the electrolyte. However, these side reactions can still occur due to humidity. Note that the layers developed in this project would need to be re-optimized for lithiation as they were optimized for proton insertion and extraction.

Throughout Chapter 5, it was shown that the ASSDs were not able to fully meet the expectations of the optical models. Section 5.3.3 highlighted the necessity to obtain a wider range of intermediate coloration levels to acquire a deeper understanding of the coloration mechanisms in the EC materials. In addition, it was previously pointed out that the characterization of the different levels of coloration was conducted in an aqueous solution, which may not fully represent the EC materials' coloration and bleaching behaviors in the developed devices. Therefore, in order to fulfill the desire to fabricate a working ASSD with optimal EC and optical performance, there is a significant need for further work in modeling and predicting the optical properties of the electrochromes under various coloration states.

A promising avenue to explore, as suggested by Tang *et al.* [121], is a new device architecture called “shoulder-by-shoulder” as illustrated in Figure 6.1. Instead of stacking all layers one upon the others, this approach involves etching the ITO-coated glass substrate to allow the two EC

materials to be deposited next to each other, separated by a layer of Ta_2O_5 . By applying the potential to the two stripes of ITO on the substrate, ions can migrate from the NiO to the WO_3 through the ion conductor.

In the present study, this concept offers a valuable potential solution as the specific optical response of each EC material can be directly observed and studied. It can be particularly useful for *in situ* ellipsometry, as it simplifies the structure under analysis while enabling the characterization of different levels of coloration without the need for chemical pre-intercalation of ions. Consequently, this method would ensure that the obtained optical properties are more representative to the actual behavior of the EC materials within the ASSDs studied in this work. This design would lower the risk of short circuits as well, since the EC layers are not superposed.

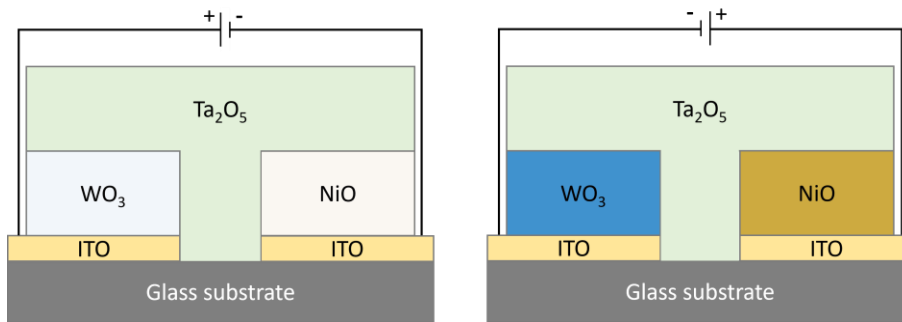


Figure 6.1: Schematic of a “shoulder-by-shoulder” ASSD in its bleached and colored states.

Adapted from [121].

This architecture was already successfully used by Qi *et al.* [122] in the fabrication of an ASSD for camera shielding. In their design, only WO_3 was used, providing two distinct areas, one colored and the other bleached, and *vice-versa*. Therefore, WO_3 served as both the cathodic EC material and the ion storage layer. The authors were able to achieve higher transparency in the bleached state compared to a standard EC device while achieving 70% transmission modulation upon coloration, thanks to the low absorption properties of the bleached WO_3 .

To address the issue of short circuits in the fabrication of ASSDs, one of the main modifications in the procedure involved reducing the deposition area for the layers during MS. Hence, the region where the electrodes are superposed was minimized, significantly lowering the probability of a

direct electrical contact between the two. This approach effectively reduced the area of concern where short circuits could potentially occur, but also reduced the size of the developed ASSDs. Another promising approach to minimize the presence of short circuits while keeping an interesting device size could be to consider a comb-like structure. This concept, illustrated in Figure 6.2, involves patterning the TCEs in a complementary structure to minimize the overlapping area.

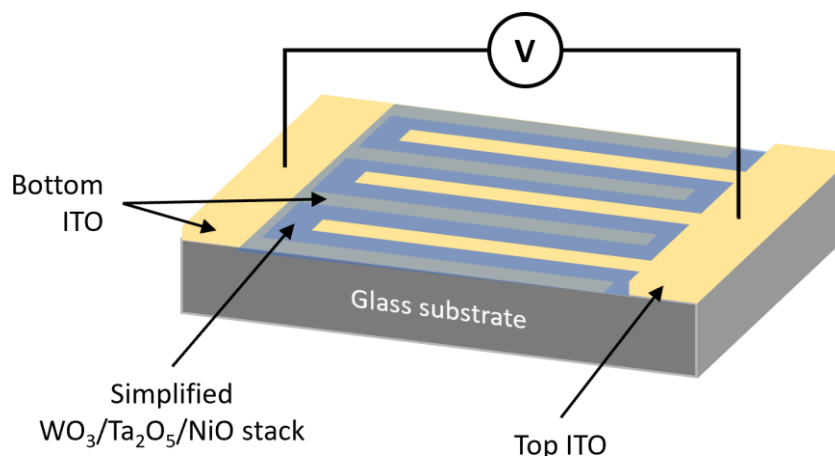


Figure 6.2: Simplified schematic of an ASSD with a comb-like structure for the ITO electrodes.

Note that the comb-like structure schematic is not to scale, the strips of both electrodes should be quite thin (a few μm wide) and must be brought closer together to ensure a sufficient conductivity as well as achieving a uniform coloration of the sample. We conducted some preliminary experiments at the Poly-Grames facilities at Polytechnique Montréal using laser etching of the ITO-coated glass. The laser parameters and the spacing between the etched lines were optimized to produce an etched area that would no longer be conductive. The first results from these experiments were promising, as shown in Figure E.1 in the Appendix. This new design would allow for the thicknesses of the different layers to be reduced, leading to faster bleaching and coloration kinetics with a lower absorption of light in the bleached state.

Finally, this project focused on achieving a reflection increase upon coloration of a WO_3/NiO ASSD. However, an alternative approach would be to use a Mg_4Ni layer instead of NiO . Indeed, it has the benefit of exhibiting an important reflection modulation upon deintercalation. However, this material was not considered at first, because it is highly sensitive to high temperatures ($> 40^\circ\text{C}$)

and high humidity ($> 80\%$). Under these conditions, it shows a quick and significant degradation of its performance and stability [123]. In addition, the fabrication process of ASSDs based on Mg_4Ni is slightly more complex as shown in Figure 6.3, which makes its fabrication more challenging.

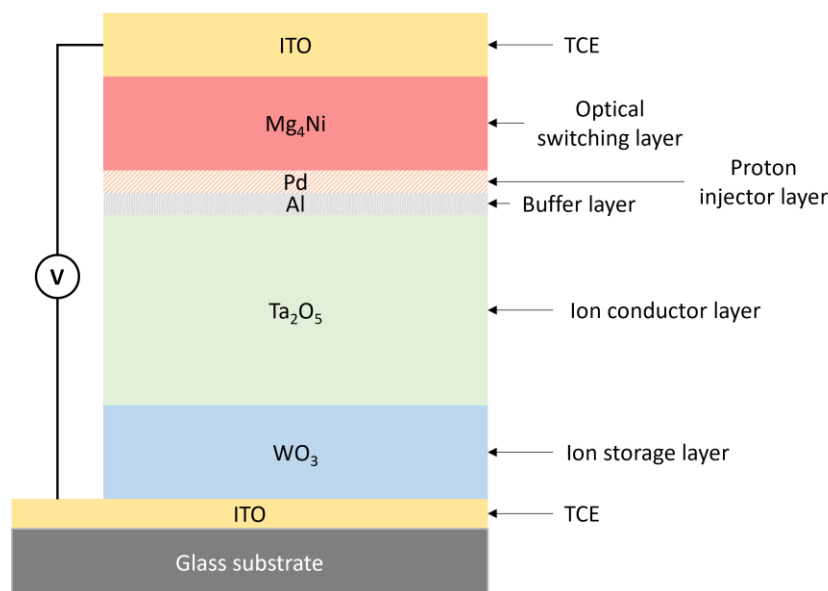


Figure 6.3: ASSD structure based on $\text{WO}_3/\text{Mg}_4\text{Ni}$ EC materials. Adapted from [124].

Indeed, the addition of a 2 nm aluminum (Al) layer was found to be critical for the durability of such devices [125]. In addition, a thin palladium (Pd) layer (4 nm [126]) is always used as a proton injector, which is crucial for the insertion and extraction of ions in the Mg_4Ni layer. Consequently, to deposit the overall ASSD illustrated in Figure 6.3 one would need to use 7 different target materials, due to the co-sputtering of Mg and Ni targets to form Mg_4Ni . Nevertheless, such a structure was reported to transition from a reflection of 19% in the bleached state to a reflection of 57% in the colored (reflective) state [127].

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APPENDIX A ELECTROCHROMIC AND OPTICAL PERFORMANCE OF THE MATERIALS DEPENDING ON THE DEPOSITION CONDITIONS

Table A-1: Summary of the important EC and optical performance of a WO₃ layer deposited under different pressures and O₂ vs Ar concentrations considering the 5th CV cycle.

Fixed condition	Tested conditions	D_i [cm ² /s]	Q_i/Q_e [%]	x [%]	ΔT_{550nm} [%]	η_{550nm} [cm ² /C]
30% O ₂ vs Ar concentration	6 mTorr	4.4×10^{-10}	331.1	7.4	5.8	18.4
	8 mTorr	8.5×10^{-9}	101.7	13.1	52.4	76.2
	10 mTorr	2.3×10^{-8}	103.5	16.9	69.1	84.3
	11.8 mTorr	2.7×10^{-8}	100.3	22.3	71.8	84.2
10 mTorr	22% O ₂ vs Ar concentration	1.9×10^{-8}	100.5	16.8	67.6	81.4
	25% O ₂ vs Ar concentration	2.1×10^{-8}	101.3	15.9	62.4	92.9
	30% O ₂ vs Ar concentration	2.3×10^{-8}	103.5	16.9	69.1	84.3
	35% O ₂ vs Ar concentration	2.9×10^{-8}	100.4	20.5	66.2	82.8

Table A-2: Summary of the important EC and optical performance of a Ta₂O₅ layer deposited under different pressures and at different thicknesses considering the 5th CV cycle.

Fixed condition	Thickness	D_i [cm ² /s]	Q_i/Q_e [%]	x [%]	ΔT_{550nm} [%]	η_{550nm} [cm ² /C]
4 mTorr	250 nm	8.0×10^{-9}	118.8	10.5	17.2	24.9
	500 nm	5.2×10^{-10}	114.8	2.6	0.1	0.7
7.5 mTorr	250 nm	4.3×10^{-8}	100.7	22.1	71.4	86.1
	500 nm	3.7×10^{-8}	100.8	20.4	63.8	88.0
	1 000 nm	3.0×10^{-8}	100.7	19	61.9	80.0

Table A-3: Summary of the important EC and optical performance of a NiO layer deposited under different pressures, reactive gas concentrations considering the 20th CV cycle.

Fixed condition	Tested conditions	D_i [cm ² /s]	Q_i/Q_e [%]	x [%]	ΔT_{550nm} [%]	η_{550nm} [cm ² /C]
8% O ₂ vs Ar concentration	6 mTorr	2.1×10^{-10}	104.4	4.8	40.6	78
	8 mTorr	1.4×10^{-10}	104.3	5.8	37.6	65.8
	10 mTorr	1.5×10^{-10}	104.5	7.7	36.6	66.5
	12 mTorr	1.4×10^{-10}	121.4	11.9	29.1	64
	15 mTorr	1.4×10^{-10}	103.8	22.3	31.9	61.8

10 mTorr	5% O ₂ vs Ar concentration	1.6×10^{-10}	101.9	9.3	39.5	65
	6% O ₂ vs Ar concentration	1.7×10^{-10}	104.4	6	41	66
	7% O ₂ vs Ar concentration	9.5×10^{-11}	104.1	5.7	34.1	72.1
	8% O ₂ vs Ar concentration	1.5×10^{-10}	104.5	7.7	36.6	66.5
	9% O ₂ vs Ar concentration	1.9×10^{-10}	104.2	9.3	41	71.6
	20% O ₂ vs Ar concentration	1.6×10^{-10}	104.1	12	34.3	73
6% O ₂ vs Ar concentration, 10 mTorr	15% H ₂ vs Ar concentration	1.3×10^{-10}	98.9	5.4	42.3	78.6
	20% H ₂ vs Ar concentration	1.1×10^{-10}	98.8	5	41.4	80.9
	25% H ₂ vs Ar concentration	2.2×10^{-10}	98.6	6.7	47.9	87.7
	30% H ₂ vs Ar concentration	1.1×10^{-10}	98.7	5	42.3	85.9
	35% H ₂ vs Ar concentration	1.4×10^{-10}	98.7	5	43.7	85.4
	50% H ₂ vs Ar concentration	1.5×10^{-10}	98.7	5.5	45	88.9

APPENDIX B IMPACT OF A POROUS ITO ON THE WO₃ ELECTROCHROMIC PERFORMANCE

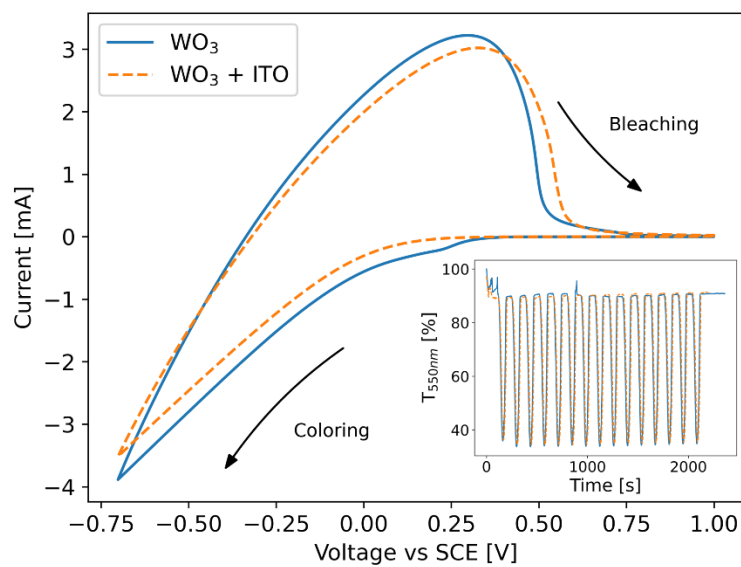


Figure B.1: Impact on the 5th cycle CV and *in situ* transmission of a porous ITO layer covering a WO₃ layer.

APPENDIX C DESCRIPTION OF THE DESIGNS AND CONSTRAINTS FOR MODELING

Table C-1: Description of different ASSD designs with the figures of merit used for optimization by modeling for both ASSDs with and without Bragg mirrors (see Figure 5.6).

ASSDs without Bragg mirror		AR ASSDs with Bragg mirrors																																									
<i>ASSD's architecture</i>	<i>Constraints</i>	<i>ASSD's architecture</i>	<i>Constraints</i>																																								
A1 <table><tr><th>Material</th><th>Thickness (nm)</th></tr><tr><td>SiO₂</td><td>83</td></tr><tr><td>Dense ITO</td><td>92</td></tr><tr><td>NiO</td><td>310</td></tr><tr><td>Ta₂O₅</td><td>535</td></tr><tr><td>WO₃</td><td>200</td></tr><tr><td>ITO (Delta)</td><td>30</td></tr><tr><td>Glass substrate</td><td>-</td></tr></table>	Material	Thickness (nm)	SiO ₂	83	Dense ITO	92	NiO	310	Ta ₂ O ₅	535	WO ₃	200	ITO (Delta)	30	Glass substrate	-	Standard design: min R_{lum_B} with SiO ₂	F1 <table><tr><th>Material</th><th>Thickness (nm)</th></tr><tr><td>SiO₂</td><td>83</td></tr><tr><td>Dense ITO</td><td>92</td></tr><tr><td>NiO</td><td>310</td></tr><tr><td>Ta₂O₅</td><td>526</td></tr><tr><td>WO₃</td><td>83</td></tr><tr><td>Porous ITO</td><td>70</td></tr><tr><td>WO₃</td><td>83</td></tr><tr><td>Porous ITO</td><td>70</td></tr><tr><td>WO₃</td><td>83</td></tr><tr><td>ITO (Delta)</td><td>30</td></tr><tr><td>Glass substrate</td><td>-</td></tr></table>	Material	Thickness (nm)	SiO ₂	83	Dense ITO	92	NiO	310	Ta ₂ O ₅	526	WO ₃	83	Porous ITO	70	WO ₃	83	Porous ITO	70	WO ₃	83	ITO (Delta)	30	Glass substrate	-	Standard design: min R_{lum_B} with 2-bilayers
	Material	Thickness (nm)																																									
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A2 <table><tr><th>Material</th><th>Thickness (nm)</th></tr><tr><td>Dense ITO</td><td>130</td></tr><tr><td>NiO</td><td>253</td></tr><tr><td>Ta₂O₅</td><td>540</td></tr><tr><td>WO₃</td><td>200</td></tr><tr><td>ITO (Delta)</td><td>30</td></tr><tr><td>Glass substrate</td><td>-</td></tr></table>	Material	Thickness (nm)	Dense ITO	130	NiO	253	Ta ₂ O ₅	540	WO ₃	200	ITO (Delta)	30	Glass substrate	-	F2 = G2 <table><tr><th>Material</th><th>Thickness (nm)</th></tr><tr><td>SiO₂</td><td>88</td></tr><tr><td>Dense ITO</td><td>95</td></tr><tr><td>WO₃</td><td>83</td></tr><tr><td>Porous ITO</td><td>70</td></tr><tr><td>WO₃</td><td>83</td></tr><tr><td>Porous ITO</td><td>70</td></tr><tr><td>WO₃</td><td>83</td></tr><tr><td>Ta₂O₅</td><td>535</td></tr><tr><td>NiO</td><td>200</td></tr><tr><td>ITO (Delta)</td><td>30</td></tr><tr><td>Glass substrate</td><td>-</td></tr></table>	Material	Thickness (nm)	SiO ₂	88	Dense ITO	95	WO ₃	83	Porous ITO	70	WO ₃	83	Porous ITO	70	WO ₃	83	Ta ₂ O ₅	535	NiO	200	ITO (Delta)	30	Glass substrate	-	Inverted design: min R_{lum_B} with 2-bilayers			
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B1 <table><tr><th>Material</th><th>Thickness (nm)</th></tr><tr><td>SiO₂</td><td>50</td></tr><tr><td>Dense ITO</td><td>82</td></tr><tr><td>NiO</td><td>300</td></tr><tr><td>Ta₂O₅</td><td>524</td></tr><tr><td>WO₃</td><td>329</td></tr><tr><td>ITO (Delta)</td><td>30</td></tr><tr><td>Glass substrate</td><td>-</td></tr></table>	Material	Thickness (nm)	SiO ₂	50	Dense ITO	82	NiO	300	Ta ₂ O ₅	524	WO ₃	329	ITO (Delta)	30	Glass substrate	-	Standard design: max ΔR_{lum} with SiO₂	G1 <table><tr><th>Material</th><th>Thickness (nm)</th></tr><tr><td>SiO₂</td><td>86</td></tr><tr><td>Dense ITO</td><td>95</td></tr><tr><td>WO₃</td><td>83</td></tr><tr><td>Porous ITO</td><td>70</td></tr><tr><td>WO₃</td><td>83</td></tr><tr><td>Ta₂O₅</td><td>529</td></tr><tr><td>NiO</td><td>200</td></tr><tr><td>ITO (Delta)</td><td>30</td></tr><tr><td>Glass substrate</td><td>-</td></tr></table>	Material	Thickness (nm)	SiO ₂	86	Dense ITO	95	WO ₃	83	Porous ITO	70	WO ₃	83	Ta ₂ O ₅	529	NiO	200	ITO (Delta)	30	Glass substrate	-	Inverted design: min R_{lum_B} with 1- bilayer								
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Glass substrate	-		ITO (Delta)	30	
			Glass substrate	-	
E1		Standard design: max $\Delta R_{lum}/(R_{lum_B})^3$ with SiO ₂	H2		Inverted design: max ΔR_{lum} with 2-bilayers
Material	Thickness (nm)		Material	Thickness (nm)	
SiO ₂	72		SiO ₂	50	
Dense ITO	83		Dense ITO	66	
NiO	302		WO ₃	83	
Ta ₂ O ₅	530		Porous ITO	70	
WO ₃	329		WO ₃	83	
ITO (Delta)	30		Porous ITO	70	
Glass substrate	-		WO ₃	83	
			Ta ₂ O ₅	555	
			NiO	200	
			ITO (Delta)	30	
			Glass substrate	-	
E2		Inverted design: max $\Delta R_{lum}/(R_{lum_B})^3$ with SiO ₂	H3		Inverted design: max ΔR_{lum} with 3-bilayers
Material	Thickness (nm)		Material	Thickness (nm)	
SiO ₂	88		SiO ₂	50	
Dense ITO	79		Dense ITO	60	
WO ₃	260		WO ₃	83	
Ta ₂ O ₅	530		Porous ITO	70	
NiO	194		WO ₃	83	
ITO (Delta)	30		Porous ITO	70	
Glass substrate	-		WO ₃	83	
			Ta ₂ O ₅	544	
			NiO	343	
			ITO (Delta)	30	
			Glass substrate	-	
			H4		Inverted design: max ΔR_{lum} with 4-bilayers
			Material	Thickness (nm)	
			SiO ₂	50	
			Dense ITO	66	
			WO ₃	83	
			Porous ITO	70	
			WO ₃	83	
			Porous ITO	70	
			WO ₃	83	
			Porous ITO	70	
			WO ₃	83	
			Porous ITO	70	
			WO ₃	83	
			Ta ₂ O ₅	536	

		<table><tr><td>NiO</td><td>429</td></tr><tr><td>ITO (Delta)</td><td>30</td></tr><tr><td>Glass substrate</td><td>-</td></tr></table>	NiO	429	ITO (Delta)	30	Glass substrate	-																																	
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Glass substrate	-																																								

APPENDIX D REFLECTION INCREASE FOR AN ASSD WITH A 1-BILAYER WO₃/ITO STACK

Material	Thickness (nm)
Dense ITO	85
WO ₃	83
Porous ITO	70
WO ₃	83
Ta ₂ O ₅	557
NiO	192
ITO (Delta)	30
Glass substrate	-

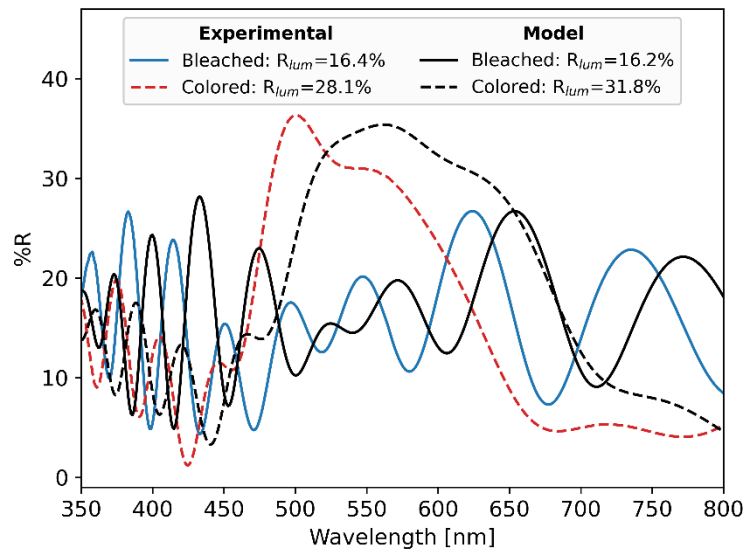


Figure D.1: Model and experimental reflection modulation upon coloration for a 1-bilayer WO₃/ITO stack incorporated in an ASSD.

APPENDIX E PRELIMINARY TEST WITH LASER ETCHING

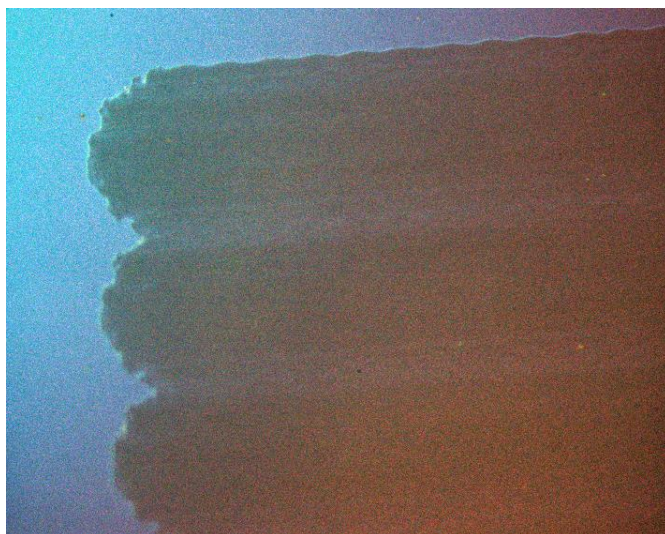


Figure E.1: Picture taken by an optical microscope (x20) of a laser etching performed at Poly-Grams on an ITO-coated substrate with the following parameters: laser defocus of 0.1 inch, 0.1 pulse/s, 85% of the laser power at 5 kHz. The etched lines were spaced by 0.0058 inches.