Optical Coatings for Automotive and Building Applications
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Abstract

Optical coatings have a long history of adding value and functionality in architectural and vehicle glazing. This talk will examine the path that has established the current “state of the art” and attempts an outlook at opportunities and challenges particularly from the drastic changes expected in the transportation sector. Energy conservation has historically been a significant driver to develop new coatings for glazing, and commoditization and large production capacity now enable proliferation of low-emissivity and solar control coatings into the world’s large construction markets, whereas new building materials (polymer membranes, flexible glass, e.g.) and functionalities (dynamic glazing, building-integrated photovoltaics, e.g.) highlight the quest for further performance improvements and innovation. While coatings on single-pane glazing are still highly relevant, many use cases have been enabled by protecting delicate coatings in laminated glass, applied window films or multi-pane insulated glazing units, all of which are very mature and with solid production capacities to support the demand for energy-efficient building glazing.

In automotive applications, improved fuel efficiency has been a motivation to adopt infrared-rejecting coatings for a while, and it will be shown that solar control functionality will be even more important to support the transition from internal combustion to electrical propulsion and even autonomous mobility. The shift towards electric propulsion changes the energy distribution of cabin climate control devices, requiring a new assessment of the role of cabin glazing. The proliferation of driver assistance systems and the trend towards autonomous vehicles will also rely on advances of optical coatings on glazing: Head-up displays have introduced an entirely new function of a windshield as a data display, and the prospect of “steering wheel optional” autonomous transportation enables the transformation of a vehicle’s windshield and windows as a large-area screen for immersive entertainment or office functionality. Constraints of such functionalities will be defined to a significant degree by the extent of autonomy. Also, attractive use cases require significant advances in display size and image quality, and may also change the expectations on privacy and security, where dynamic glazing may play a significant role.

Overall, optical coatings for architectural and automotive glazing will continue to rely on the proliferation of mature coating and manufacturing technologies to achieve global energy conservation goals, while new materials and transportation modes demand continued innovation from optical coatings to deliver new user experiences and capture attractive new market opportunities.

Keywords: Optical Coatings, Solar Control, Photovoltaics, Dynamic Glazing, Autonomous Driving, Electrical Vehicles, Energy Conservation

1 Introduction

Optical coatings have a long history of adding value and functionality in architectural and vehicle glazing. This talk will examine the path that has established the current “state of the art” and attempts an outlook at opportunities and challenges particularly from the drastic changes expected in the transportation sector. The discussion will focus on optical coatings on applications with a significant transmissive function (primarily glazing), and exclude optical coatings for mirrors or reflectors.

2 A brief history of optical coatings for automotive and architectural glazing

Although optical coatings have a very long recorded history for optical components and lenses, a breakthrough development in the automotive and architectural glazing field is the introduction of laminated “safety” glass in 1936. While not a coating process in itself, it is
a crucial enabler to many successful coating applications as we will describe later. The energy crisis motivated the adoption of passive thermal control through low-emissivity and infrared-reflecting (IRR) coatings, initially in architectural glazing to promote energy conservation; adoption of IRR coatings in automotive glazing followed in 1998.

What can be described as a first example of multi-functional glazing occurred in 1988 with the first market introduction of automotive head-up displays integrated into a windshield. Around 2000, the architectural field adopted multifunctionality with self-cleaning windows and building-integrated photovoltaics (BIPV).

2005 saw the advent of active “dynamic glazing” (DG) in the form of electrochromic (EC) and polymer-dispersed liquid crystal (PDLC) devices. At that time, most EC devices had good spectral and shading control but relatively slow switching time that was more acceptable in architecture than in automotive sectors, while PDLC devices are fast-switching but without significant spectral control, making them suitable mainly for privacy applications.

The first fast-switching EC device for an automobile was introduced in the 2012 model year.

Around 2015, the second generation of multi-functional glazing was introduced with a proliferation of infotainment integration into glazing (often through advanced head-up displays in automotive, augmented-reality / virtual-reality (AR/AV) functionality through the melding of windows and displays).

It is interesting that once a fundamental glazing coating functionality takes hold in the market, it generally remains available with continued market demand.

3 Coating Integration

3.1 “Exposed” functional coatings

Before we investigate the wide field of “encapsulated” functional glazing coatings, it should be recognized that there are many applications that require coatings exposed to the elements. Self-cleaning photocatalytic anatase TiO$_2$ coatings, rain/ice-repellant hydrophobic or anti-fog hydrophilic coatings, pyrolytic ITO low-emissivity coating or anti-reflection coatings are the most prevalent examples. These coatings have severe demands on environmental stability and mechanical robustness that often require compromises in their intended functionality.

3.2 Glazing Architectures to enable most coating functionalities

In most use cases, a glazing coating must be protected from environmental impacts (chemical and mechanical) to achieve optimum performance. Three variants to accomplish this will be reviewed.

3.2.1 Laminated glass

Laminated glass consists of two glass panes that are laminated together, typically with a polymer poly-vinyl-butyral (PVB). This construction allows the incorporation of coatings at a glass/PVB interface, or within the PVB. Coatings at the glass/PVB interface are called “direct-coatings”, and the coating is applied to the glass surface prior to bending (yielding good uniformity but requiring thermal compatibility with the bending process), or to coat the glass after bending (allowing for a wider range of coatings, but requiring considerations for the glass curvature in coating equipment and uniformity control). The vast majority of architectural low-emissivity and IRR coatings are produced as “direct-coatings” as well as many IRR coatings for windshields.

Another option to integrate functional coatings into laminated glass is to deposit the coating on a transparent polymer substrate in roll-to-roll processes that is then sandwiched between two sheets of PVB and laminated between the two glass panes. While the assembly process may be more demanding, this approach may have advantages from a logistics perspective, and can accommodate very high radii of curvature as compared to most direct-coat options.

3.2.2 Insulated Glazing Units (IGUs)

The thermal barrier performance of windows can be dramatically improved by introducing an
insulating gas space between two glass panes. Most modern architectural windows in colder climates achieve remarkable energy conservation performance by means of this concept. Since the cavity is hermetically sealed and typically filled with a noble gas (in addition to a desiccant), the inner glass surfaces can be coated with very sensitive but high-performance silver-based low-emissivity coatings. Those low-e coatings are reaching the physical limits of their emissivity performance, and added thermal insulation requires additional cavities. The resulting increase in weight from the additional glass panes has given rise to a concept where the inner glass panes are replaced by thin, low-e-coated and tensioned polymer films that provide comparable thermal performance at significantly reduced weight.

3.2.3 Window Film

Window film provides a pathway to retrofit or add functionality to an already existing glazing surface without having to replace a window. Window films enable a wide range of functionalities such as glare control, solar control, intrusion protection/security, privacy, decoration, or electromagnetic shielding. They can be found in both architectural and automotive applications.

Most window films consist of a complex layered structure that may contain several coated films bonded with a laminating adhesive, a mounting adhesive and disposable liner, and possibly a hard coat for scratch protection.

There are many techniques to impart functionality onto a window film, including dyeing, wet- or vacuum-coating. High-performance films are often vacuum-coated with complex multi-layer structures especially for high-end solar control performance. Wet-coated nano-particle films can add effective infrared absorption for solar control window films with high visible transmission ($T_{\text{vis}}$).

For solar control films, a key performance metric is “selectivity”, which is the ratio of $T_{\text{vis}}$ over Solar Heat Gain Coefficient (SHGC). For an automotive solar control windshield application that needs to meet a regulatory $T_{\text{vis}}$ of 70% at the lowest possible SHGC, a high selectivity is therefore desired.

4 Architectural Glazing Coatings - New Paths for Energy Efficiency

Optical coatings for energy efficient glazing – particularly in architecture – are very mature, fully commoditized, and highly effective with high adoption rates, and they are often mandated by building regulations. However, a few concepts should be mentioned to highlight opportunities for further energy efficiency improvements.

4.1 Building-integrated Photovoltaics (BIPV)

Rooftop-mounted unitized solar panels are highly commoditized and ubiquitous, but there is still an opportunity for façade-integrated PV, and integrating PV into windows is an intense field of study that has gained some commercial traction. A primary challenge for glazing is that in order to achieve visible transmission, a significant and attractive portion of the solar spectrum is no longer available for PV conversion, resulting in low output efficiency, although several PV materials systems exist that can provide this functionality.

4.2 Emissive Films

In cooling-dominated regions, there is an interest to reduce air conditioning loads by introducing heat-dissipating (high-emissivity) coatings. Such coatings are spectrally optimized to provide radiative sky cooling without consuming electricity. While current demonstrations of this concept showcase opaque coatings for rooftops due to the combination with a highly effective solar reflector, it is conceivable to introduce such functionality into glazing.

4.3 Coatings for innovative glazing materials – ETFE

Ethylene Tetrafluoroethylene (ETFE) film (and closely related derivative formulations) is a construction material that enables transparent, lightweight, and durable roofing and façades with appealing design characteristics.
The ETFE film can be incorporated in a range of construction concepts (membranes and pillows) that have been showcased in a number of high-profile projects such as sports venues, malls, public spaces and even energy-conserving façade retrofits in virtually all climate zones. The motivations and appeal of this construction material have been described elsewhere at this conference.

With glass as the functional competitor to ETFE, there currently is a significant performance gap between the two options regarding solar control functionality. Glass offers many mature coating options for a large market, whereas coating ETFE is technically challenging, and provides a relatively limited market size. Therefore, there is a need for the development of functional coatings that enable broader adoption of ETFE as a construction material, and there are several industrial and publicly funded initiatives underway to not only improve solar control functionality, but also add PV or dynamic glazing functions to ETFE to increase its competitiveness versus glass, and to leverage the light-weighting and low-embodied-energy benefits of the ETFE architectural concept.

4.4 Coatings for innovative glazing materials – Flexible Glass

The introduction of ultra-thin flexible glass at commercial scale by several manufacturers is a significant opportunity to combine the advantages of roll-to-roll coating with significant advantages that glass has over traditional polymer films: mechanical robustness, temperature tolerance, and gas barrier performance.

Significant efforts are underway to integrate roll-to-roll coating processes on flexible glass, and current applications aim at high-value applications such as OLED displays and organic PV; for glazing applications, BIPV or electrochromics may be of particular interest.

4.5 Outlook: Optical Coatings in Architecture

The “State-of-the-Art” in architectural optical coatings can be characterized by the commoditization of low-emissivity, solar control and photovoltaic coatings. They benefit from economics-of-scale, often driven by regulatory requirements and standardization, and enable broad global adoption of energy-efficient construction methods to address global climate change challenges.

Current development focus aims at integrating PV into glazing, and to generate market traction for dynamic glazing, particularly electrochromic glazing.

Future focus areas may include: market introduction of “fast” dynamic glazing to enable new use cases, innovation in coatings for ETFE membranes to bring performance closer to glass and enable proliferation of light weighting and low-embodied-energy benefits, the introduction of passive cooling from emissive coatings on glazing, and product introductions of BIPV and dynamic glazing based on flexible glass through roll-to-roll concepts.

5 Solar Control – the Basics

Looking at the extreme climate zones in the contiguous USA helps with the understanding of basic solar control concepts that are important for architectural and automotive solar control coatings.

The northern areas – zones 6 and 7 as identified by 2009 IECC standards – resemble “heating-dominated” areas. Southern areas – zones 1, 2 and 3 – are “cooling dominated”.

Windows in the “heating-dominated” zone can help conserve energy if they harvest as much solar energy as possible to provide passive solar heating. At the same time, they should minimize heat loss from the inside of the building. Therefore, a bandpass filter that transmits the complete solar spectrum (up to 2,500 nm) while reflecting 24°C blackbody radiation is desirable. This can be accomplished by a single-silver low-emissivity dielectric / metal / dielectric stack.

In contrast, windows in the “cooling dominated” zone aim to minimize the air conditioning load by minimizing the solar energy admitted through the window while still providing visible transmission. A bandpass filter with a limited transmission band in the wavelength range of 340-780 nm is desirable, and ideally maximum reflection particularly in the solar spectrum between 780 and 2,500 nm.
An infrared-reflecting (IRR) stack made of multiple silver layers between dielectric spacers accomplishes this economically for practical glazing applications.

6 Automotive Glazing – Energy Conservation and Added Functionality

As described earlier, automotive glazing is a significant market for optical coatings, with a wide range of applications. We will review established and mature products, and will also identify some potential changes in coating functionality that may be motivated by other technological advances in the automotive sector.

6.1 Automotive Infrared-reflective (IRR) glazing

Windows constitute a significant portion of the envelope of a vehicle’s passenger cabin of a car, and the solar radiation transmitted into the cabin can contribute to significant solar energy absorption and heat-up that requires ventilation or cooling. Modern vehicles often have air conditioners that are designed to remove the excessive heat in the cabin, and the air conditioner is an energy-consuming “load” of around 3 kW on the engine that impacts fuel efficiency by up to 20%. Because air conditioners typically work “on-demand”, reducing cabin heat-up by restricting transmitted solar energy also reduces the energy consumed by the air conditioning unit, and improves fuel economy. This is very similar to the use case for architectural coatings in “cooling-dominated” climate zones, and consequently, narrow-bandpass IRR coatings are used to address this issue, especially in the windshield and front side lites where a high $T_{vis}$ is mandated by regulations. IRR coatings are the most effective way to prevent cabin heat-up. Yet, IR absorbing coatings often are still effective as a vehicle in motion can conduct a significant portion of the absorbed energy to the outside air rather than re-radiating it into the cabin, and current industry glazing metrics recognize this. For automotive optical coating designers, this enables a wider range of energy-conserving coating design options that can respond to the varying demands of e.g. a windshield vs. a sunroof while still integrating other demands such as solar shading or privacy.

Although eventually not implemented, there have been regulatory efforts to mandate the use of solar control coatings in order to advance fuel efficiency performance. Such coatings are in wide use today – both as an original equipment manufacturer (OEM) options as well as in window film retrofits - as glazing areas expand, driven by shallower slopes of windshields for improved aerodynamics and increasing roof glazing areas.

6.2 Glazing in the post-ICE vehicle era

The recent shift to augment or replace internal combustion engines (ICE) with electric propulsion may pose a change in the functionality of automotive glazing to improve fuel efficiency or extend driving range. As described above, the physics of solar cabin heat-up still apply to non-ICE vehicles, and the motivation to mitigate the impact of air conditioner loads on the energy consumption – i.e. battery drain – through IRR coatings still applies.

Cabin heating – on the other hand – presents a new challenge to manage the range of an electric vehicle. Unlike an ICE vehicle – where about 18% of the energy is used for propulsion, and about 80% is waste heat that can easily be used to heat a cabin on demand without impacting fuel efficiency –, a battery-electric vehicle has a propulsion efficiency of about 60%, with practically no waste heat usable for cabin heating, and consequently such vehicles require a dedicated electrically powered heating system. It has been shown that the heating load may be up to twice that of air conditioning, and can result in a driving range reduction of up to 30%. More efficient heat pump systems (as compared to older positive temperature coefficient (PCT) heaters) can help improve this load on the battery, but the underlying challenge that both heating and cooling reduce the range of a battery-electric vehicle still remains, and it may be conceivable that functional coatings for cabin glazing may help address that challenge.
An additional motivation for reducing battery drain from climate control needs in battery-electric vehicles may come from the emerging trend toward autonomous driving. Early prototypes consumed up to 4.5 kW for the sensors and computers to enable autonomous driving, modern systems may consume approximately 2.5 kW, with a goal to eventually reduce this to 0.5 kW.

The motivation to extend the range of electrical vehicles may also motivate a trend towards light-weighting, which can possibly be supported by applying functional coating on thin flexible glass, as well as opportunities to integrate photovoltaics into roofing or glazing surfaces to facilitate supplemental battery charging.

6.3 Functional glazing aspects of autonomous driving

Autonomous driving is an emerging automotive technology trend that may affect the use and design of optical coatings in vehicle windows. Opportunities to address the energy consumption aspects of autonomous driving have been addressed above, but there are also some optical performance aspects that will be described here.

SAE (J3016) categorizes six levels of autonomy, from no automation (level 0) to driver assistance systems enabling some automated driving modes (example: cruise control) to full automation during all driving modes (level 5). Any level below 4 requires a human to at least serve as a fall-back in case the automated systems fail, for many systems within 10 seconds.

For glazing functionality, this can be translated into the option to re-define the function of a windshield for level 5 to become something other than a “see-through” windshield: perhaps an immersive entertainment or data display, or enabling complete privacy from electrochromics. Lower autonomy levels still need to maintain T_vis at 70% when driver intervention is required, so the privacy or immersive entertainment functionality will be much more restricted.

Data visualization on the windshield is already available in head-up displays, and various systems are on the market, from combiners (that project an image on an additional transparent surface) to direct projectors with fairly large and complex imaging to the prospect of fluorescent displays that may have a very large field of view. All these technologies often achieve functionality through optical coatings, such as the suppression of ghost images, luminous efficiency improvements as well as haze and glare control.

Other aspects relate to the accommodation of driver assistance systems (cameras, transponders, sensors) that may be installed on or near automotive glazing and must not be impaired by functional coatings such as IRRs. Transmission of radio signals from windshield-mounted toll collection transponders has been identified as a particular issue for silver-based IRR coatings that significantly attenuate RF signals.

If the television industry serves as a reference point for trends, the transition from projection (cathode ray tubes and rear-projection) to flat panel LCD and OLED displays may perhaps have an equivalent transition in the automotive realm, where current projection technology may be succeeded by transparent LCD or transparent OLED integration into glazing surfaces, which has already been demonstrated at a concept stage. Such a change in the automotive glazing field would obviously provide a broad range of opportunities for optical coatings.

7 Conclusions

Optical coating technologies for architectural and automotive glazing are firmly established in the market, and the various coating designs and integration options have enabled energy-efficient glazing on a massive scale. While commoditization will help proliferate these solutions to broader markets, additional functionality is anticipated. For architecture, these may be expanding current niche applications such as BIPV and dynamic glazing as well as working with new construction materials such as ETFE membranes or flexible glass. For automotive uses, solutions are needed that cater to the specific power consumption aspects of
battery-electric vehicles as well as responding to needs and opportunities of the trend towards autonomous driving. To fulfil these market needs, coating designers and product developers in the glazing field are called to continuously innovate and create new business opportunities.

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Electrically heatable Low-E glass
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There is remarkable temperature difference between the glass inside surface and indoor air when temperature is like a normal winter day in Nordic Countries. Remarkable energy can be saved by using electrically heatable glass in façades in cold climate conditions. The glass surface is heated just to room temperature or 1-2 degrees higher and this brings not only energy savings but also comfort near the window area to compare to fan coils or radiators. An important factor is that by using electrically heated glass the building can get more square meters in use as we do not need radiators or fans in the façade window area. This is remarkable savings to utilize room as radiator or fans took 30 up to 100 cm area from window wall.

Besides of current solutions, there are no guaranteed solutions to prevent coldness and cold draught inside building. Fan coils and radiators blow 55 °C hot air by natural or forced convection during a cold winter day. This may almost double the heat loss compared to a system where the window inside surface temperature is heated with electrical heated glass to room temperature 21 °C. Heating is done by utilizing a low-e coating inside in IGU or inside laminated units using 110 or 220 volts.

Pure façade purchase cost with electrically heatable glass is more expensive than façade without heatable glass. However, glass façades in cold climates can be made at remarkable lower costs with electrically heatable glass compared to the old system where we need to use radiators or fans. Total savings from this new façade can be up to 50%. Electrically heatable glass can be used also to melt snow load or avoid condensation.
Coating of ETFE – solar shading for architectural applications
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Abstract

In 1982 the first building to be clad with an ETFE (ethylene tetrafluoroethylene) foil system was completed for the Burger’s Zoo in Arnhem, The Netherlands. One of the principle characteristics of ETFE is high transparency across the entire solar spectrum from UV light (280 nm – 380 nm) over visible light (380 nm – 780 nm) to near IR radiation (780 nm – 3000 nm). This performance is ideal for provision for plant growth resulting in transmission of nearly 90 % of photosynthetically active radiation (PAR). For human habitats the broad band high transmission rate may result in heating up of inside areas, thus enhancing the energy consumption required for air conditioning. In order to enhance user comfort and reduce cooling loads the foils have to be specially treated or coated. ETFE foils have a low surface energy (23 mN/m) which inhibits surface adhesion offering maintenance advantages from self-cleaning effects but presenting considerable challenges for the design and application of stable coatings. Additionally, when installed as a building cladding system ETFE foils undergo significant in-service deformation, both plastic and elastic, as result of designed stabilising pre-stress and in response to dynamic environmental loadings. Plastic deformation is an additional safety factor for ETFE cushion cladding systems. Corresponding serviceability limit states (SLS) as well as ultimate limit states (ULS) are currently under discussion in the norm committee for a European standard for membranes and foils, CEN/TC 250 Structural Eurocodes, WG 5 Membrane Structures [1,2]. Coatings have to cope with this specific performance. A well-balanced relation between adhesion and cohesion is a fundamental requirement. The pigments have to remain stable on the foil surface even under conditions of multiple cyclic deformation in the range of both elastic and plastic deformation due to short term but high blast loads. This article will provide a brief introduction into the development of coating and printing on ETFE in particular, as well as an introduction into different techniques for solar shading of ETFE cladding systems in architectural buildings. In order to allow for quality assessment of these coatings taking into account elastic and plastic deformation of the target material, a new test procedure for coated ETFE will be introduced. Keywords: ETFE- ethylene tetrafluoroethylene, Texlon® systems in architecture, solar shading, quality assessment of coatings, transmission and reflection

1 Introduction

Extruded films formed from ethylene tetrafluoroethylene (see Figure 1) were first identified as an ideal material for transparent building envelopes by Dr. Stefan Lehnert, founder of Vector Foiltec, in 1982 and were subsequently developed as the primary component of a multi-application building cladding system under the brand name “Texlon®”. The first project built by employing this technology was the Mangrove Hall of the Burger’s Zoo in Arnhem, The Netherlands, in 1982.

Fig. 1: Ethylene tetrafluoroethylene chemical structure [3].

The basis of a standard Texlon® multilayer system is an airtight cushion formed by welding together a minimum of two ETFE foil layers held within an extruded aluminium alloy perimeter frame. The cushion is connected to a low pressure (250 Pa) air supply which raises the internal pressure pre-stressing the ETFE foils and thereby imparting structural stability to the whole system.
A pressure feedback control maintains a constant internal operating pressure regardless of fluctuations in external temperature and atmospheric pressure. The number of ETFE foil layers can be modified from two up to six layers to improve the thermal performance (reduce U-values). A more detailed introduction to the technology can be found in “ETFE – Technology and Design” by Annette LeCuyer [4]. A graphic representation of the system arrangements as described is shown in Figure 2.

![Fig. 2: 3D cutaway perspective of a Texlon® 3-layer ETFE cladding panel.](image)

Early architectural projects utilising ETFE cladding technology were built with uncoated high transparency clear ETFE films. Clear, uncoated foils have high levels of transmittance across the full band width of the solar spectrum (see Figure 3).

![Fig. 3: Transmission T and reflection R of 250 µm ETFE foil up to 20.000 nm wavelength.](image)

ETFE cladding panels can sustain structural stability with a high surface area to perimeter ratio and due to their low mass can be supported by lightweight open structures, a significant advantage for sustainability and costs. However, in combination these properties can result in high total solar energy transmission through clear ETFE foil cladding systems and therefore careful consideration should be given to any requirement for solar control.

The first ever architectural application of a coating applied to an ETFE film for solar shading was for the atrium roof at the Schlumberger Research Institute in Cambridge, UK, in 1992, (Fig. 4 below). This was achieved by the development of a rotogravure, roll to roll printing process applied on ETFE film by Vector Foiltec. The print pattern employed was a relatively low density ink DM 4:65 arrangement (4 mm dot matrix covering 65 % of the foil surface). The shading performance though effective was limited and thus supplementary blinds were still required in front of the windows on the ground floor below. Fluoro-copolymer foils such as ETFE have self-cleaning properties due to their low surface energy (in the case of ETFE approximately 23 mN/m), which inhibits the adhesion of other materials or particles to the foil surface. This material behaviour created considerable challenges to the development of stable coating systems for the modification of ETFE foil transmission properties.

Despite these technical difficulties it can be seen from the detailed view of the print pattern produced in 1992 that after 23 years exposure to environmental conditions (Fig. 4) the coating applied is still in good condition (Fig. 5).

![Fig. 4: ETFE atrium roof Schlumberger Research Institute, Cambridge, UK, outer foil printed on inner surface, print pattern DM 4:65, light optical density ink.](image)
In order to not destroy the self-cleaning effect of the outer foil and for protection of the ink, printing is always applied on side two, i.e. towards inside the cushion. Whilst the primary driver for the development of coatings to ETFE foils is to modify the transmission characteristics for solar radiation coatings have also been utilised for purely aesthetic purposes. In 1998 Vector Foiltec applied what was then state of the art coating ETFE technology in the realisation of ‘The Meteorit’ a sculpture designed by André Heller for the centenary of RWE, and exhibited in Essen, Germany (Fig. 6 below).

After corona treatment of what would become the inner surface of the ETFE foil to raise the surface energy and enhance adhesion, a reflective fluoropolymer lacquer was applied by hand. The printed areas were limited to the inner surfaces of the sculpture to protect the lacquer from the external environment.

The development of high reflectance printing for the control of solar radiation on ETFE foils was the key technological advance that expanded the range of application to that of a universal cladding product for high transparency roofs and façades. An extensive ETFE roofing system was fundamental to the success and growth of ‘The Avenues Mall’, the largest shopping mall complex in Kuwait and the second largest in the Middle East. Phase III ‘The Grand Avenue’ encloses a main boulevard and adjoining side streets under 25,000 m² of ETFE roof (see Fig. 7) creating a comfortable conditioned space with the experience of an open sky above which is not only a major commercial success but has become a social hub for the whole region [5,6]. Since completion of Phase III in 2010 further Phases IVa and IVb have now been completed creating a range of further commercial and social spaces protected from the harsh external environment under a total of nearly 100,000 m² of Texlon® ETFE roofing system, which is shown in Fig. 8.
Despite the high external temperatures experienced in Kuwait in this building typology, with full height large volume spaces, a low thermal transmission (U-value) for the roof cladding system is not a primary consideration because of temperature stratification effects. Hot air rises forming a stable layer immediately beneath the roof of comparable or greater temperature than that outside. Temperature gradually decreases moving downwards to the comfort zone at ground level below. During night time when temperatures outside the building are lower, loss of thermal energy outwards through the roof is a beneficial effect reducing daytime cooling demand.

The necessity for control of radiative solar gain is however paramount. The reflective coatings used at The Avenues Mall are a third generation medium opacity ink applied in a DH 7:84 print pattern to the inner surface of the uppermost foil, (7 mm hexagonal matrix covering 84 % of the foil area).

For the 3-layer system (200 µm – 80 µm – 200 µm), with outer foil printed on the inner side, the performance is given in Table 1:

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<th>UV light</th>
<th>Visible light</th>
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### 2 Printing and Coating on ETFE

Printing and coating on foils made from ethylene tetrafluoroethylene (ETFE) is technically highly demanding for both the formulation of the lacquer systems and the physical coating process. This is consequent to both the material characteristics of the foil itself and the wide range of environmental stresses that the printed foil must endure as the primary element of a building envelope cladding system.

The principle material features of the ETFE foil that impact on adhesion, cohesion and the physical and chemical stability of the applied coatings both during application and in-service are:

1. A very low surface energy of less than 23 mN/m, which inhibits the normal mechanism involved in surface adhesion.
2. A high potential for elastic and plastic deformation under load – 400 % elongation can occur under mono-axial stress before structural failure.
3. A relatively low melting point of approximately 280 °C.
4. A significant degree of water vapour permeability – for a 200 µm ETFE foil vapour permeability is approximately 2 g/(m²d).

5. A high degree of transparency to UV radiation – for a 200 µm ETFE foil transparency to UV radiation is approximately 80 %.

The range of extreme environmental stresses that a completed ETFE based cladding system may be required to endure include:

1. Temperature - ETFE cladding systems have been installed in a wide range of climatic zones around the world and have to be capable of enduring external temperatures as low as -40° C and as high as + 50° C.

2. Wind Loads - external building envelopes are subject to high wind loads of varying gust durations and load distributions causing high and unequal stresses to be induced in the ETFE foils.

3. Snow loads – create high long duration loading scenarios maintaining high stresses in the ETFE foils over extended periods of time.

4. High humidity, rainfall and condensation – depending on circumstances can cause vapour pressure gradients in both directions across ETFE cladding membranes.

5. Partial water ponding – certain partial deflation scenarios can result in localised water ponding resulting concentrated loads and associated stresses.

6. Folding, bending and buckling - during the production process, transportation and installation of the ETFE cushions and single layers repeated or sustained folding and buckling can occur.

Both sets of parameters define the provisions and requirements for coating formulation and its consequent mechanical and chemical properties, printing process and treatment systems:

1. Before coating the surface of ETFE foils must be pre-treated by either corona or plasma treatment to raise the surface energy. The best results regarding adhesion have been identified at a surface energy of around 56 mN/m. In order to achieve these values ETFE foils can be corona treated one side directly during the extrusion process. Unfortunately the effect of the corona treatment will decrease with time it is therefore strongly recommended that this treatment is undertaken directly before coating.

2. After coating the ink must be dried by the controlled application of heat within a drying channel. Temperatures should however not be allowed to exceed 70°C as the mechanical stability of the ETFE foil is very sensitive to temperatures and deformation can occur if the temperature is too high or unevenly distributed.

3. The roll to roll process induces longitudinal stress in the foils. However, elongation deformation is not acceptable as multiple short lengths of foil must be welded together to form larger sheets for cushion production. The print patterns must align perfectly across welds and specific marks are printed along roll edges to ensure alignment is correct prior to welding.

4. As the primary component of a cladding system foils will be deformed elastically and to some degree plasticly during service life. Coating adhesion must be sufficiently robust to withstand shear stresses at the interface between foil and pigments whereas cohesion has to perform sufficiently elastic in order to resist disruption or cracking of the matrix.

5. The coating must remain stable under 100 % humidity within a cushion under simultaneously high external temperatures. Despite pressure from water vapour permeability neither degradation nor generation of plaque due to micro-cracks and micro-channelling is acceptable.

6. The coating must have long-term UV stability

7. The coating must retain adhesion and cohesion under dynamic stresses from wind loading across a wide material temperature range of -40° C up to +80° C.

8. The coating must retain adhesion and cohesion in areas of sustained high strain and peripheral buckling induced by snow loads.
9. The coating must retain adhesion and cohesion in localised zones of high strain caused by folding and buckling during welding as well as production and installation activities.

10. To facilitate many production welding scenarios it is necessary to be able to remove coatings precisely from localised areas of foil. Despite the need for extremely high levels of stability in the many circumstances cited above it must also be possible to economically, effectively and safely remove coatings when required as part of the cladding production process.

### 2.1 Development of ink for printing on ETFE

In close cooperation with a company specialising in the research and production of varnishes and paints Vector Foiltec developed a coating system for use with ETFE foils in 1990 and undertook rigorous testing of its application in an automated gravure printing production process. The first architectural application of this printing system was in the ETFE atrium roof at the Schlumberger Research Institute in Cambridge, UK, in 1992. Eight years later the technology was transferred to a German printing company and since then has become the standard system for printing on ETFE for architectural applications. Accordingly, this technology is now used by nearly all suppliers of ETFE cladding systems. With the exception of zoological and botanical buildings where high levels of solar transmission are required, printing is employed in almost all ETFE cladding installations in order to control incoming solar radiation. Vector Foiltec have continuously worked on further optimization of printing ink formulation for exclusive use in their ETFE cladding products with a particular emphasis on enhanced system performance, environmental sustainability and occupational health and safety. In 2010 major advances were achieved in improved optical density and reflectivity in close cooperation with a company in Austria, a specialist in the printing of security features on bank notes, which contributed extensive laboratory and research resources. The new ink was based on an acrylic lacquer as opposed to the previously used fluoropolymer resin lacquers enabling the use of much less harmful solvents for the removal of printed ink for welding purposes. The continuous improvement over time in the solar control capabilities of specialist ETFE printing inks is demonstrated in Table 2. (The more recent acrylic based system is indicated by the prefix H and the former resin system by the prefix R.)

| R01249 | 41,9 | 41,7 | 41,4 | 30,8 | 39,9 | 39,7 | 0,56 |
| R78185 | 9,7  | 12,6 | 12,8 | 38,2 | 51,5 | 51,1 | 0,47 |
| H318105| 6,6  | 7,2  | 7,1  | 48,4 | 57,7 | 54   | 0,43 |
| H560110| 2,5  | 2,7  | 2,6  | 53,9 | 56,6 | 55,4 | 0,4  |

For a standard 3-layer ETFE cushion system similar to that deployed in Phase III ‘The Avenues Mall’ Kuwait (200 µm transparent outer foil, 80 µm transparent middle foil, and 200 µm transparent inner foil, outer foil printed on the inner face with DH 4:84, 4 mm hexagonal matrix with 84% coverage), the g-values calculated for the 4 different print systems would be:

- g-value (R01249) = 0.46
- g-value (R78185) = 0.25
- g-value (H318105) = 0.21
- g-value (H560110) = 0.18
It should be noted that transmission and reflectance characteristics for both the visible portion $T_{vis}$ and the solar transmission $T_{sol}$ are closely aligned. Reduced solar gain consequent to increasing the percentage of ink surface coverage and/or reflectivity will result in a similar reduction in visible light transmission with these coating systems.

2.2 Texlon® “Vario” system

The Texlon® “Vario” system was developed to provide a cladding solution that could react to changing demands for solar control or visible light transmission in response to customer requirements or variations in the external environment. The system can be triggered to switch modes by automated sensor driven controls or manual push button operation.

Basic system function is illustrated in Fig. 9 (see also Fig. 10).

In the standard ‘Vario’ arrangement the two outermost layers of a three layer panel are printed with a complementary offset print on their inward facing surfaces. The middle or innermost printed layer can be moved upwards to rest against the uppermost printed layer or down to meet the bottom layer by pumping air from one side of the middle foil to the other creating a pressurised chamber either below or above the middle foil.

In the open position the middle foil is pushed downwards and diffuse and direct incident light can pass through the clear areas of foil between the printed patterns on both layers of foil. Moving the printed middle layer upwards to meet the upper layer partially or wholly covers the clear areas of each foil with the printed layers of the other reducing the total area of clear foil through which solar radiation can pass. Variation in the total area of print on each of the two foil layers and the degree of overlap in the registration of the two layers can be used to adjust the design performance of any system in both open and closed modes to meet the requirements of local environmental conditions.

The optical and the thermal performance of a Texlon® vario system with one of a number of different print pattern combinations (SQM 200-197:45 dark) for open and closed position is given in table 3.
Solar light transmission is 10 % in the closed position and 26 % when open and the associated g-value or Solar Heat Gain Coefficient SHGC are 0.14 closed and 0.37 open. It should be noted that in the standard arrangement the middle foil is always in contact with the uppermost or bottom foil in the closed or open position respectively and therefore for the purpose of thermal insulation this is always a single chamber system with a corresponding U-value of around 2.78 W/m²K.

### 3 Test procedures for coatings on ETFE

As outlined in section 2.0 above the demands on the stability performance of ETFE coatings for building cladding applications are severe, yet it must still be possible to efficiently remove these coatings as part of the production process. Probably the most demanding performance capability of all is the retention of adhesion and cohesion under long and short term deformation, typically up to 5 %, due to dynamic environmental loading. Classic accelerated weathering test methods within climate chambers simulating rain, alternating temperatures and UV impact are therefore not sufficient for the determination of ageing performance of coatings on ETFE foils. Formerly, standard test methods such as EN ISO 4892 [7,8] have been applied and revealed no difference in performance for a range of ETFE coatings, however in-service external exposure in mock-ups and some historic installations has led to cases of print degradation or loss of adhesion. Therefore, new test procedures had to be developed in order to cope with the demands for long-term stability on ETFE foil systems.

#### 3.1 Long Term Corrosion Test

A 15 mm wide strip of coated ETFE is loaded by a weight fixed at one end of the stripes (see Fig. 11) inducing a stress of approximately 17 N/mm² [9]. The weight is 6.5 kg and the thickness of the ETFE foil is 250 µm.

![Fig. 11: Weight for creation of 17 MPa load on an ETFE stripe of 15 mm width.](image)
The test assembly is placed into a climate chamber for 10 days at a temperature of 80° C. Tension in the strip must be maintained permanently, as the strip will elongate over time and let the weight come to rest at the bottom of the container the metal stick must be rotated on a regular basis for the period of the test. The print is tested by applying the Tesa-/Tape-Test [10, 11]. Because the strip has undergone significant elongation (356 % over the period of the test) the optical density is of course reduced. No changes, no cracks, no delamination or defects caused by Tesa-Cross-Cut-Test were found for any of the H samples, neither for H 318105 nor for H 560110 print system.

A comparison with the former ink showed significantly enhanced stability for the new H lacquer.

### 3.2 Hysteresis Tests

When installed in roof and façade cladding systems ETFE foils undergo frequent exposure to wind loads imposed by a wide range of wind speeds. Gusting wind speeds are typically 40 % higher than basic wind speeds. For the purpose of analysis [12] wind gusts are generally considered to last for about 3 seconds. Texlon ® ETFE cushion systems are stabilised by an inner air pressure of approximately 250 Pa inducing a permanent pre-stress load of approximately 4 MPa to the outermost foils. Single layer systems are pre-stressed to approximately 6 MPa. In order to simulate these load conditions a hysteresis test procedure using a mono-axial tensile test machine has been designed. In order to simulate extreme wind conditions the load cycling was determined to be between 9 MPa and 18 MPa. The strain-stress diagram is shown in Figure 16.

![Fig. 16: Strain-stress diagram of 250 µm ETFE foil, 300 cycles; test for print stability.](image)
The diagram also illustrates the ageing performance of the ETFE material itself. Cyclic loads will cause reduction of strain with increasing number of cycles even under 18 MPa loads. The ETFE foil becomes stiffer with mechanical ageing [13]. After the test strips with the coating under examination have been subjected to 300 load cycles, they are exposed to accelerated weathering tests according to standard norms [7, 8]. The load test of various coated samples from different printing companies gave evidence regarding long term stability of the coatings.

3 Results and Discussion

Over the last 28 years printing and coating technology on ETFE foils for architectural applications has improved significantly. Performance regarding reflectivity and optical density has been improved by more than a factor of 2. For a standard 3-layer ETFE cladding system comparison of performance achieved from the first generation printing systems with the best systems currently available demonstrate that g-values have improved from initially around 0.46 to as low as 0.18. It should be mentioned that foils with embodied pigments introduced into the foil matrix prior to extrusion are also available from ETFE foil manufactures. These embodied pigments can also contribute to the selective modification of transmission and reflection properties. When these coloured ETFE foils are used in combination with printing the potential for solar control is further expanded and this opens an even wider range for tuning the ETFE foil cladding systems according to local project related requirements.

Even though there have been approaches towards selective solar shading by applying sputtering technologies on ETFE foils no solution is currently available to the construction market. This is mainly a consequence of the physical properties of ETFE foils, which are both permeable to water vapour encouraging oxidation, and flexible leading to micro cracking and delamination of the metallised coatings. For the time being therefore solar shading in ETFE systems will still be linked to a reduction in visual light transmission. In order to simulate ageing effects of coatings on ETFE foils specific methodologies have been developed for laboratory based tests. These tests not only take into account loss of adhesion of print or other types of coating on ETFE foil systems resulting from cyclical stretching of the foils under environmental loadings but are essential for the understanding of the in-service ageing characteristics of the material itself. In contrast to most of the other materials used for the building cladding systems foils and membranes are constantly deflected by environmental loads, which has a major impact on ageing behaviour and must therefore always be taken into consideration. Standard Test procedures and methods specified in the current standards are not sufficient for quality control of textile membranes and foil treatment systems.

References


[10] ASTM F 2252/ Sun Chemical-Hartmann PV 01, Self-adhesive tape test (tesa test)


Vacuum coating on polymer films for outdoor applications
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Abstract

This paper discusses functionalization of ETFE webs by vacuum roll-to-roll deposition of permeation barrier layers and highly conductive transparent electrodes for outdoor applications. A 100 nm thick gas barrier layer (zinc-tin-oxide – ZTO) and a 60 nm thick transparent conductive layer stack (indium-tin-oxide – ITO 25 nm – Ag 10 nm – ITO 25 nm) achieve a water vapor transmission rate of 0.01 g/m²d (at 38°C/90% r.h.) and sheet resistance of < 6 Ω/sq on a commercial grade ETFE film. However, the elastic properties of ETFE as well as its creep-behavior require specific attention during roll-to-roll processing and for design of the functional layer stacks. In consequence, layer thicknesses and material selection must be balanced between functional performance and the ability to survive deformation of the polymer web. This paper compares functional performance and crack formation under strain load of different layer stacks on both PET and ETFE substrates.

Keywords: ETFE, permeation barrier, membrane architecture, transparent electrode, coatings for outdoor application

1 Introduction

A major trend in modern architecture is the use of large transparent and translucent façade and roof elements to make time spent in buildings like airports, stadiums and shopping malls more pleasant [1-3]. Fluoropolymer webs like ethylene tetrafluoroethylene (ETFE) are a lightweight alternative to glass providing a long lifetime and resistance to weathering for integration in such membrane elements [1].

ETFE films with surface functionalization would allow energy harvesting (e.g. solar modules) and active heat management systems (e.g. electrochromic cells) in membrane roofs or façades.

Therefore, the films require coating with thin metal oxide layers. In an earlier study, we demonstrated roll-to-roll deposition of single layers, multi-layer systems on ETFE and the challenges related to processing [4]. The low dimensional stability of ETFE requires adapted process parameter to avoid damage to the thin oxide layers. In contrast to many other materials, the inorganic material ZTO shows sufficient adhesion on ETFE. Furthermore, reactively sputtered ZTO achieves reasonable water vapor barrier performance on PET [5].

However, integration of electronic functionality (e.g. solar cells, electrochromic cells) requires a transparent conductor on the ETFE surface as well. This paper discusses the integration of ZTO permeation barrier layers with ITO and oxide metal oxide (ITO – silver – ITO) coatings to create a functional substrate for large area flexible electronics on ETFE with respect to both functional performance and mechanical stability in a linear strain test.

2 Experimental

2.1 Polymer substrates

The substrate was a 100 µm thick ethylene tetrafluoroethylene web ET6235-Z provided by NOWOFOL® Kunststoffprodukte GmbH & Co. KG. The reference material was polyethylene terephthalate PET Melinex ST504 from DuPont Tejin films with a film thickness of 125 µm.

2.2 Coating processes and equipment

All coating experiments were done in the vacuum roll-to-roll coater labFlex® 200 with two single magnetrons and a dual magnetron system (DMS) (Fig. 1). Zinc-tin-oxide (Zn2SnO4, ZTO) and indium-tin-oxide (ITO) layers as well as ITO-Ag-ITO stacks were deposited on a coating width of 200 mm. ZTO was applied using a reactive sputtering process with zinc/ tin metal alloy targets (52 wt-% zinc and 48 wt-% tin) [6]. Layer thickness was controlled by adjusting the plasma power and the web speed. A ceramic ITO target (90 wt-% indium and 10 wt-% tin) was used
in a DC-sputtering mode with a gas mixture of oxygen and argon to deposit transparent electrode layers.

![Image](image.png)

Fig. 1: Scheme of the roll-to-roll coater labFlex® 200 according to [7].

2.3 Characterization methods

Water vapor transmission rate (WVTR) was measured using a carrier gas based measurement device with a coulometric sensor from BRUGGER Feinmechanik GmbH. The device has a lower limit of detection of $1 \cdot 10^{-3}$ g/(m²d). The measurement area was 78 cm² and the measurement conditions were set to 38°C / 90% relative humidity (r.h.) for all measurements. Layer resistivity was measured using an FPP 5000 Four Point Probe from Vecco Instruments. The crack formation was examined in-situ by a stereomicroscope while stretching the coated samples in a tensile test according to DIN EN ISO 527. From that, a crack onset strain was derived which indicates the elongation of the film which exhibits the first visible occurrence of cracks.

3 Results and Discussion

3.1 Performance of single layers

Fig. 2 compares water vapor transmission rates of ZTO single layers deposited on ETFE with such on PET. As shown in earlier publications the WVTR decrease with increasing layer thickness for both, coated PET and ETFE [4]. A homogenous, large area deposition on ETFE is challenging due to an inhomogeneous substrate thickness leading to inhomogeneous web tension and surface temperature. This affects the maximum applicable plasma power (and therewith productivity) for sputter coatings on ETFE. Similar functional layer properties (WVTR; adhesion; optical performance) were observed for a plasma power range between 1…2 kW. However, local thermal damage leads to wrinkle formation on the roll and prevents productive usage of a plasma power of 2 kW and higher. Currently, a set of optimizations of the intrinsic properties and homogeneity of the ETFE are evaluated with the goal to increase applicable plasma power.

![Image](image2.png)

Fig. 2: Water vapor transmission rate of ZTO single layers on PET and ETFE. For ETFE a variation of plasma power was used from 1 kW (2.4 W/cm²) up to 2 kW (4.7 W/cm²).
Table 1 compares the sheet resistance of ITO and multilayer electrodes on ETFE and PET (without a ZTO barrier layer). An increased layer thickness of ITO results in a lower sheet resistance.
Table 1). The lowest value was around 30 Ω/sq for a 150 nm thick ITO layer on both substrates. However, such a high layer thickness results in a very low crack onset strain of less than 1%. Membrane technologies expect much higher crack onset strains for roof or façade applications. An oxide metal oxide layer-system with 25 nm ITO 10 nm silver and again 25 nm ITO (total multi-layer-thickness 60 nm) enables a much lower sheet resistivity of less than 6 Ω/sq and a crack onset strain of 1.5%.

Table 1: Comparison of sheet resistivity for ITO and multilayer electrodes on ETFE and PET.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Layer and layer thickness</th>
<th>Sheet resistivity [Ω/sq]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>ITO (50 nm)</td>
<td>115</td>
</tr>
<tr>
<td>PET</td>
<td>ITO (150 nm)</td>
<td>32</td>
</tr>
<tr>
<td>PET</td>
<td>Multilayer (25 nm - 10 nm - 25 nm)</td>
<td>6</td>
</tr>
<tr>
<td>ETFE</td>
<td>ITO (50 nm)</td>
<td>124</td>
</tr>
<tr>
<td>ETFE</td>
<td>ITO (150 nm)</td>
<td>35</td>
</tr>
<tr>
<td>ETFE</td>
<td>Multilayer (25 nm - 10 nm - 25 nm)</td>
<td>5.5</td>
</tr>
</tbody>
</table>

3.2 Performance of multilayer systems

Applications like organic solar cells and electrochromic cells need a layer stack of ZTO and electrode to protect the device against water vapor and oxygen and to provide a transparent anode for the device. The deposition of an ITO layer or a multilayer electrode on top of ZTO does not negatively affect the water vapor transmission rate (Fehler! Ungültiger Eigenverweis auf Textmarke.). The sheet resistivity of single electrodes on ETFE is comparable to such on an ETFE / ZTO pre-coated films. This was shown on PET, too.

Fig. 3: WVTR of ZTO single layers and layer stacks of ZTO with 50 nm ITO (blue points), respectively, ZTO with 60 nm multilayer electrode (25 nm ITO – 10 nm Ag - 25 nm ITO) on ETFE.

However, a stack of two inorganic materials like ZTO and ITO results in a lower crack onset strain because the total thickness of the full inorganic stack is relevant.

Fig. 4 shows the crack onset strain in dependence on the total stack thickness of both...
ZTO single layers and ZTO / electrode stacks. An increased ZTO-layer thickness results in a lower crack onset strain. With a top layer of ITO on ZTO, crack onset strain is reduced further and finally results in 0.6% for a layer stack of 100 nm ZTO and 150 nm ITO. This is significantly lower than required by the application as even processing of subsequent functional layers at elevated temperatures (e.g. deposition and curing of a printed organic semiconductor such as PEDOT:PSS) results in a film strain of 1 ... 2%.

The WVTR of this stack is 0.023 g/m²d and the sheet resistivity is 34 Ω/sq. Both WVTR and sheet resistance are increasing drastically when exceeding the crack onset strain in a linear strain test thus losing application relevant performance.

Combining ZTO with an oxide-metal-oxide electrode leads to lower total stack thickness. A higher crack onset strain of 1.2 % with a sheet resistivity of 5 Ω/sq and a WVTR of 0.01 g/m²d was observed using a 100 nm ZTO layer with an multilayer electrode (25 nm ITO – 10 nm Ag – 25 nm ITO).

Fig. 4. Comparison of crack onset strain for different ZTO layer thicknesses compared to multi-layer stacks of ZTO and ITO respectively oxide-metal-oxide-electrodes on ETFE. The multi-layer thickness means the total thickness of deposited inorganic material.

4 Conclusion

This paper successfully demonstrates the deposition of layer stacks with ZTO and ITO or oxide-metal-oxide-electrodes, respectively. While application relevant functional performance was shown, the crack onset strain – as a merit for material failure under strain load – decreases with increasing layer thicknesses. Application demands a crack onset strain larger than 1.5% ... 2% which is only achieved with a stack with total thickness < 60 ... 80 nm. However, reducing in ZTO layer thickness yields higher water vapour transmission rates. Balancing the functional performance and the ability of the coating to withstand mechanical load and strain is one major aspect of application relevant improvement and development of functional polymer web for outdoor application with both gas barrier performance and transparent electrode.

Acknowledgements

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References


The effect of sputtering growth parameters on the electrochromic properties of WO$_3$ thin films grown on Ga-doped Zinc oxide

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Abstract

In this work, the influence of the sputtering power and pressure on the electrochromic properties of WO$_{3-x}$ are studied. WO$_{3-x}$ layers with a thickness of 160±5 nm were grown on Ga-doped Zinc Oxide coated glass substrates (6x6 cm$^2$) by RF magnetron sputtering. A thickness sensor controlled thicknesses of the WO$_{3-x}$ layers. A series of WO$_{3-x}$ films were deposited at different sputtering powers changing from 45 W to 90 W with a constant sputtering pressure of 5 mTorr. As the second series, the sputtering pressure was varied from 5 mTorr to 13 mTorr at a constant sputtering power of 45 W. Electrochromic measurements were studied by a cyclic voltmeter, chronoamperometry and lifetime cycle measurements. Decreasing the WO$_{3-x}$ sputtering power from 90 W to 45 W leads to an increase with the coloration efficiency from 42.1 cm$^2$/C to 70.3 cm$^2$/C. The film grown at 45 W shows 63% transmission modulation at 630 nm wavelength. The increase in the WO$_{3-x}$ sputtering pressure from 5 mTorr to 13 mTorr results in a decrease in bleaching times from 15 to 5 seconds. The WO$_{3-x}$ films grown at different pressure yield similar coloration efficiency of 69±2 cm$^2$/C and about 63% optical modulation at 630 nm wavelength.

1 Introduction

Electrochromic materials have attracted great interest because of their potential application areas such as smart windows for energy efficiency building, information displays and rearview for automobiles [1-3]. Comparing with the other inorganic electrochromic materials WO$_3$ is the preferred one because of its high coloration efficiency, short switching time and better electrochromic stability [4-8]. Electrochromism can be defined as the changing of the color stimulated by redox reaction. When electron and ions charged or discharged into electrochromic thin films, it results in a change in electronic structure by moving the Fermi levels. This creates an absorption of the light therefore the electrochromic thin films switch from transparent (bleach) to absorbing (color) state or vice versa. This reaction is reversible meaning that when the applied voltage polarity is reversed, the electrons and ions move to the other direction than before which let the electronic structure to turn back to the real states. For tungsten oxide (WO$_3$), electron transitions occur between W$^{5+}$ and W$^{6+}$ atomic states which is causing absorption in the layer [9-12]. As indicated the electron and ion insertion/extraction in the electrochromic layer is a critical factor and these are depending on the layer properties such as microstructure, crystallinity and porosity of the layer [13-16]. These properties of thin film mostly controlled by the growth conditions. In the literature, there are some studies dealing with the influence of sputtering growth conditions like substrate temperature, film thickness, total gas pressure and oxygen gas flow rate on the electrochromic properties of WO$_3$ layer [17-19]. Electrochromic layers can be obtained by different techniques such as thermal evaporation, ion beam sputtering, CVD and magnetron sputtering [20-23]. In this study, the magnetron sputtering technique was preferred for deposition because of its simplicity, relatively low cost, the ability to obtain good quality films and its benefits for up-scaling applications.
This paper focuses on the growth of WO$_{3-x}$ by RF magnetron sputtering and the investigation of the sputtering deposition parameters such as growth power and pressure on electrochromic properties of WO$_3$. The relations between total pressure and growth power with the film properties accordingly the electrochromic properties have been clarified.

2 Experimental

WO$_{3-x}$ films were deposited on Ga-doped ZnO coated glass substrate by RF magnetron sputtering. At first Ga-doped ZnO (5% Ga) (GZO) films were deposited by pulsed DC magnetron sputtering on 2 mm glass substrate using an in-line magnetron sputtering. The thickness of the GZO is in the rage of 330 nm±5nm. Afterwards the coated glasses were annealed at 250 °C for two hours at 10$^{-3}$ mBar pressure. After annealing, a sheet resistance of 16-17 Ω/sq was recorded by four-point probe measurement. These GZO samples with the size of 6x6 cm$^2$ were used as substrates for the deposition of WO$_3$ thin films by RF magnetron sputtering. For WO$_3$ growth, a 5 cm-diameter metallic target of a pure tungsten has been used and the depositions took place in a mixed of 50 % Ar/ 50 % O$_2$ atmosphere. Two sets of WO$_{3-x}$ layers with a thickness of 160±5 nm were prepared. A thickness sensor controlled thicknesses of the WO$_{3-x}$ layers. A series of WO$_{3-x}$ films were deposited at different sputtering powers changing from 45 W to 90 W with a 15 W increment. The pressure of 5 mTorr was kept constant. As the second series, the sputtering pressures were 5 mTorr, 7 mTorr, 10 mTorr and 13 mTorr at a constant sputtering power of 45 W. The target to substrate distance was kept constant at 7.5 cm for each deposition. The system was evacuated to a base pressure of less than 5x10$^{-6}$ torr prior to the growth. Two separate gas flow controllers were used to monitor flow rate of Ar and O$_2$. The structural properties were studied by X-ray diffractometer (XRD) with CuKα radiation (λ: 1.5418 Å). X-ray reflectivity (XRR) measurements were performed to evaluate the density of the layers. Optical characterization was done by Perkin-Elmer UV-VIS-NIR spectrophotometer in the wavelength range of 280-2500 nm. Electrochromic measurements were studied using a cyclic voltammetry (CV) on a potentiostat. 0.3M Lithium perchlorate-propylene carbonate (LiClO$_4$-PC) solution was used as an electrolyte. Chronoamperometry (CA) and lifetime cycle measurements were performed to evaluate the amount of the intercalated charge and the coloring and bleaching times, respectively. CV measurements were conducted between +1 V and -1 V with the scan rate of 20 mV/s. CA measurements were done at a fixed potential of 1 V (coloration) and -1 V (decoloration) with 20 s steps for the coloration and bleaching times. A silver-silver chloride (Ag/AgCl) and a platinum wire were used as a reference and counter electrodes, respectively.

3 Results and Discussion

3.1 The effect of sputtering power on electrochromic properties of WO$_3$ grown on GZO

Fig. 1(a) and (b) represent the transmission measurements and XRD scans of WO$_3$ grown on GZO substrates at different power, respectively. Fig. 1(a) shows transmission curves of uncoated GZO and WO$_3$ coated GZO samples. GZO coated glass substrate has about 85% transmission in the visible range and the transmission decreased about 5% after growing 160 nm thick WO$_3$ layers. There is no big difference in transmissions with WO$_3$ samples grown at different power. All these are indicating that WO$_3$ thin films are fully oxidized. All the X-ray diffraction peaks seen in Fig.1(b) is from the GZO substrate and there is no diffraction peak is observed related with WO$_3$. This shows that the WO$_3$ thin films have amorphous structure.
Fig. 1: a) Transmission curves of WO$_3$/GZO thin films and uncoated GZO substrates and b) XRD scans of WO$_3$ grown at different powers.

Table 1: Growth conditions of WO$_3$ samples grown at different power.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Power (W)</th>
<th>Pressure (mTorr)</th>
<th>Film Density (g/cm$^3$)</th>
<th>Optical Modulation (630nm)</th>
<th>Coloration Efficiency (630nm)</th>
<th>Porosity (%) ($\lambda=630$nm)</th>
<th>Reversibility (%)</th>
<th>Growth rate (A/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>45</td>
<td>5</td>
<td>6.9763</td>
<td>63.1</td>
<td>70.3</td>
<td>25.47333</td>
<td>97</td>
<td>0.14</td>
</tr>
<tr>
<td>W2</td>
<td>60</td>
<td>5</td>
<td>7.1741</td>
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<td>52.0</td>
<td>23.24667</td>
<td>89</td>
<td>0.16</td>
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<tr>
<td>W3</td>
<td>75</td>
<td>5</td>
<td>7.1975</td>
<td>55.1</td>
<td>51.2</td>
<td>22.27333</td>
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</tr>
<tr>
<td>W4</td>
<td>90</td>
<td>5</td>
<td>7.2384</td>
<td>29.6</td>
<td>42.1</td>
<td>21.82667</td>
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</tbody>
</table>

Fig. 2(a) and (b) show CV and CA measurement results of WO$_3$ samples, respectively. The measurements were performed between -1 V and +1 V applied voltage. As seen in Fig. 2(a) the current density is decreasing with increasing the growth power from 45 W to 90 W. This clearly indicates that with increasing power the structure of the layer is changing which is making the charging of the layer harder. When we look at in Fig. 2(b), similar behavior can be seen in a way that the bleaching time is shorter for the sample grown at lower power of 45 W [9]. In chronometer results sample grown at 90 W shows shorter bleaching and coloring times but even seeing a charging/discharging, this sample did not reveal a clear electrochromic behavior. In other words, after the first cycle of the CV, there are some charges trapped in the film and full discoloration was not observed [10, 24]. Therefore, the times for coloration and discoloration are not indicating the time need for full coloration and discoloration of the layer. This can clearly be seen in Fig. 3(a). Sample grown at 45 W shows a larger change in transmission between color and bleached states. However, sample grown at high power of 90 W has the lowest transmission modulation. Low power grown sample (45 W) reveal a transmission
modulation as large as 63.1%. However, it decreases with increasing the growth power as seen in Fig. 3(b). For high power grown sample (90 W), the transmission modulation is recorded as low as 29.6%. The optical density, which is associated with the ability of absorption of the layer, is also decreasing with increasing growth power. This means the number of the active $W^{5+}$ atoms decreased because of the increase in number of trapped Li ions at higher growth power [10, 24].

In Fig. 4 (and in Table 1) coloration efficiency and film density variation against growth power is given. Coloration efficiency, which is one of the most important parameter for the evaluation of electrochromic behavior, is recorded as high as 70.3 for sample grown at 45 W. A decrease in coloration efficiency from 70.3 to 42.1 cm$^2$/C is observed with increasing the growth power from 45 W to 90 W. Film density, which is evaluated by using XRR measurement, change with growth power is shown Fig. 4. An increase of the film density with increasing the growth power is observed (Table 1). The porous structure of WO$_3$ grown at lower power facilitates the Li-ion and electron charging/discharging into/out of the layer more easily. In other words, the trapping of the Li ions in the crystal structure is reduced which helps to keep the active $W^{5+}$ atoms as active and enhance the electrochromic efficiency [10, 24].
3.1 The effect of sputtering pressure on electrochromic properties of WO$_3$ grown on GZO

In this part, the results based on the samples grown at different total pressure will be explained. Details of the growth condition are given in the experimental part and in Table 2. On these samples, XRD and spectrophotometer measurements were performed. Similar with the power series samples, WO$_3$ thin layers revealed an amorphous structure and the glass/GZO/WO$_3$ system has about 85% transmission in the visible range (graph is not given).

Fig. 5 presents the cyclic voltammograms (a) and chronoamperometer (b) measurement results of WO$_3$ samples grown at different total pressure. The CV and CA measurements were conducted between ±1 V vs Ag/AgCl potential. In Fig. 5(a) there is a clear difference observed with threshold voltage at which value the current density starts to decrease towards zero after reaching the maximum current density during coloration [9].
While the threshold voltage is higher than 1 V for the sample grown at 5 mTorr (the hysteresis loop is not closed completely at +1 V) for sample grown at 10 mTorr the threshold voltage is decreased to 0.3 V. This means that a small voltage of about 0.3 V is enough for fully charging of the WO$_3$ layer grown at 10 mTorr and 13 mTorr.

Concerning the CA results given In Fig. 5(b), it can be seen that with pressure increase, the time required for a full charging/discharging (full coloration/bleaching) is decreasing. Especially the discharging time is much smaller for the sample grown at 10 and 13 mTorr.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure (mTorr)</th>
<th>Power (W)</th>
<th>Optical Modulation (630nm)</th>
<th>Coloration Efficiency (630nm)</th>
<th>Coloration Efficiency (630nm)</th>
<th>Response Time (sec)</th>
<th>Reversibility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>5</td>
<td>45</td>
<td>63.1</td>
<td>70.3</td>
<td>63.1</td>
<td>11</td>
<td>15</td>
</tr>
<tr>
<td>W5</td>
<td>7</td>
<td>45</td>
<td>63.3</td>
<td>68.6</td>
<td>63.3</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>W6</td>
<td>10</td>
<td>45</td>
<td>66.2</td>
<td>67.9</td>
<td>66.2</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>W7</td>
<td>13</td>
<td>45</td>
<td>63.8</td>
<td>71.3</td>
<td>63.8</td>
<td>8</td>
<td>6</td>
</tr>
</tbody>
</table>

Fig. 5: CV and CA results of WO$_3$ thin layers grown at different pressure (a) cyclic voltammograms (b) chronoamperometers of WO$_3$ thin films (inset show full chronoamperometry measurement results).
During CA measurements transmission variation of the film was measured by an in-situ spectrophotometer (Fig 6). The measurements were performed at 630 nm wavelength. In order to show clearly, full coloration and bleaching curves for the results of 5 mTorr and 10 mTorr are given in Fig. 6(b). A big difference with the coloration and bleaching times are seen. With increasing the pressure from 5 to 10 to mTorr, the coloration times decreased from 11 to 6 seconds and the bleaching times are decreased from 15 to 5 seconds. Detailed results are given in Table 2. In Fig. 7, coloration efficiency and transmission modulation results are shown. Transmission modulation between the color and bleach states is in the range of 63%. There is no big influence of the growth pressure on the transmission modulation seen. In addition, the coloration efficiency, which shows the performance of the electrochromic layer, is also not varying too much with changing the growth pressure. If we sum up the pressure series results, it can be concluded that the growth pressure has a big influence on the coloring and bleaching times of WO$_3$ layers. However, there is no big influence on the other electrochromic behavior. This can be explained in a way that at all pressures used in this study the sample can be fully charged and discharged with Li atoms. As we see in Table 2 the reversibility is in the range of 97±1% for all samples [25].

![Fig. 6: In-situ transmission measurement results.](image)

![Fig. 7: Coloration efficiency and transmission modulation versus growth pressure.](image)

For deeper understanding of the growth pressure effect on the WO$_3$ electrochromic properties long lifetime measurements were made. CA measurements together with in-situ transmission measurements (630 nm) were performed for a cycle number of 500. At 5 and 10 mTorr samples the coloration efficiency show a similar drop with the number of cycle. For both samples, the coloration efficiency decreased about 6 cm$^2$/C after 500 cycles. However, the transmission modulation shows a different trend for samples grown at 5 and 10 mTorr. While 10 mTorr sample shows only 7% decreased after 500 cycle, 5 mTorr sample shows about 15%
decrease with transmission modulation. For 5 mTorr sample transmission modulation decreased sharply between 100-200 cycles. On the other hand, the decrease with transmission modulation is slower for 10 mTorr and the overall decrease is less. This can be explained with the porosity of the layer. The sample grown at a higher pressure can be more porous because of the fact that at high pressure the energy of the W adatoms reaching to the substrate surface is less. The decrease with the adatom energy can be explained with the scattering of the Ar ions that directed to the target surface and the scattering of the ad atoms in plasma. W atoms with less energy lead to the formation of more porous thin films on a substrate [16].

Fig. 8: Transmission modulation and coloration efficiency versus number of cycles. CE and TM represents coloration efficiency and transmission modulation, respectively.

4 Conclusions

The effect of the sputtering power and the pressure on WO$_3$ electrochromic properties were investigated. A strong influence of the growth power on the coloration efficiency and the transmission modulation were observed. At low power of 45 W the coloration efficiency is found as much as 70.3 $\text{cm}^2/\text{C}$. Growth pressure mainly changed the coloration and bleaching times. Coloration and bleaching times decreased from 11 to 6 seconds and 15 to 5 seconds with increasing the growth pressure from 5 to 10 mTorr. In addition, with increasing the growth pressure the lifetime of the WO$_3$ electrochromic layer got better.

References


Spectrum-Selective and Photocatalytic Coating towards Smart Glass

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Abstract

Advanced coatings are revolutionizing the traditional functionalities of window glass. Herein we present a multifunctional coating which not only selectively allows the desired optical spectrum to pass through it, but also utilizes the undesired ultraviolet light to activate its photocatalytic property. The coating could find promising application in smart glass coatings.

Keywords: Glass coating, Multifunctional, Spectrum selective, Photo catalysis

1 Introduction

Glass is widely used in fenestration for not just buildings but also vehicles and airplanes all over the world, however new development is needed for next generation window glass [1]. For example, ordinary glass allows not only visible light but also a large amount of ultraviolet (UV) and infrared (IR) light to pass through it. UV light can cause accelerated aging and damage to human skins and furniture. And allowing IR light to pass through the window makes the windows being important channel for heat loss or heat gain [2], which requires excess energy for heating or cooling so as to maintain a comfortable temperature inside the enclosed space. Energy consumption and environment deterioration are two of the most urgent challenges mankind is facing today [3]. Therefore, next generation glass technologies which can contribute to energy saving and tackle environmental pollution would be highly desirable in modern architecture and automobile industry.

Herein, we present a special coating on glass which not only selectively allows certain spectrum to pass through it, but also helps to eliminates harmful species thanks to its photocatalytic properties.

2 Experimental

Physical vapor deposition (PVD) method was used to grow the special coatings on glass substrates. The microstructure of the coatings were revealed by high resolution transmission electron microscope, and the properties of the coatings were studied by optical transmittance spectra. Photocatalytic performance of the coatings were demonstrated by methyl orange degradation experiments under UV light illumination.

3 Results and Discussion

3.1 Spectral selectivity

Fig 1.: Transmittance spectrum of coating on glass.

The special coating we developed has very favorable spectrum-selective features. As shown in Fig. 1, the coating is highly transparent with an average transparency above 96% in visible light range, thus allowing enough visible light to pass through it. At the same time, the coating shows low transmittance across the UVA spectrum region (300 nm – 400 nm in wavelength), which is not absorbed by the ozone thus it is the most relevant UV light that needs to be blocked off. Besides, the transmittance of the coating drops abruptly beyond the short wavelength IR (SWIR). And both the transmittance edges in the near UV and IR range can be modulated by engineering the coating, thus the transmittance spectrum of the coating can be further optimized according to the applications.
3.2 Photo catalysis

![Comparison of photocatalytic performance of three different coatings on glass](image)

Besides its spectrum-selective feature, our coating also exhibits photocatalytic properties. As demonstrated in Fig 2, under illumination of UV light, the coating is able to degrade organic contaminants into less harmful species through photocatalytic process. It is worthy to note that the photocatalytic performance of our special coating is about 2.5 times as much as that of the reference coatings (coating 1 and coating 2), which makes our coating a promising candidate to crack down the harmful contaminants in both liquid or gas environment. Therefore, our coating can work as a passive “cleaner” that helps to improve the water and especially air quality, which becomes an urgent issue in many developing countries.

4 Conclusion

In conclusion, we present a multifunctional coating on glass, which shows both spectrum-selective feature and photocatalytic property. These favorable properties enable our coating great potential in smart glass coating applicable in architecture, automobile, aerospace, etc.

Acknowledgements

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References

Hard coatings for the production of automotive glazing plastic parts - a short historical review with a proposal how to overcome present obstacles successfully in near future

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Abstract

To reduce weight and to enhance freedom in design and functionality polymeric materials like polycarbonate (PC) were used to produce e.g. ophthalmic lenses and displays or automotive glazing parts for cars to save energy by replacing glass as a basic mass volume material. But the polymers need a hard surface which has to be added by coatings. A first approach was the application of lacquers: first pure organic e.g. acrylic polymer based systems – later on hybrid systems containing inorganic micro- or nano-sized particles made of silicon dioxide or quartz to enhance the poor hardness of acrylic materials with new siloxane based products to an acceptable performance. Then sol-gel- and water based lacquers widely replaced organic solvent based systems to come to a more environmental-friendly process and it became the standard production method in industry. Starting in the Middle of the last century vacuum- and plasma-based processes were developed to overcome the drawbacks of lacquers. First approaches were high vacuum thermal evaporation of SiO\(_2\) and SiO in modified standard batch coaters. A lot of projects, using different Plasma-CVD coating systems and plasma sources and mainly hexamethyldisiloxane (HMDSO) as a precursor followed and are reviewed in a few examples. After this, decades of work to implement an environmental-friendly, cost-effective production process a suitable solution is now available for indoor and other applications, which do not need UV-protection. The PCVD process based on the linear scalable „PlasmaLine“-MW-Source allows high deposition rates of > 7 µm/min. on 0.6 sqm of SiO\(_2\) with TMDSO or other siloxane precursors fulfills all requirements for that. To adapt additional features like decorative metallization, AR-top coats or integrated U V-protection for outdoor applications well known PVD processes - e.g. sputtering of ZnO or even more promising ZnOS - have to be combined with the hard coat process. The BMBF projects MINERVA and NANO-UV could demonstrate that all of the single process steps needed are available now, but they have at least to be fit together. The summarized historical experience will help to accomplish the work in addition with some new experimental results which will be able to optimize life-time durability by well enhanced cracking- stability and although reduce temperature impact. So a calculable effort in time and costs for the process and product development is a realistic perspective on the way of the implementation of a new coating technology for a large number of innovative products in the near future.
Electrochromic devices offer fascinating possibilities for lighting and building climate control as they allow for actively controlling light and energy throughput in a wide range. In the last decades the technology matured from an academic research topic to commercially available products especially in the field of architectural glazing. For the main optically active electrode, generally tungsten oxide $\text{WO}_3$ is used. For the counter electrode different materials such as $\text{NiO}:\text{H}$, $\text{TiVO}_x$ and $\text{IrO}_2$ are employed. However, still a need for high performance, environmentally friendly and low cost materials exists. We present such new potential materials for active layer and counter electrode deploying our serial (Mega-tron®) and parallel co-sputtering technologies for film deposition.
Chromogenic Polymers – materials with controllable optical properties

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Abstract

The wide application potential of chromogenic thin films and coatings becomes obvious when having a closer look on selected examples, such as packaging films with intrinsic temperature-controlled sensor properties, adaptive sun protection systems, electrochromic panes or pressure sensitive coatings. This paper summarizes recent development directions and active principles of functional polymers with thermochromic, thermotropic, electrochromic and piezochromic properties. It gives a brief introduction on possibilities for controlling the optical properties of these materials.

Keywords: chromogenic polymer, thermochromic film, thermotropic material, electrochromic pane, piezochromic material

1 Introduction

By external stimulation with light, temperature, mechanical forces or electric potential, chromogenic materials can change their color. This class of materials might also exhibit a deepening or fading of the color or show transitions between a transparent and a scattering or a reflective state. This is due to a stimulated change of the optical properties of these materials. It results in a change of the absorption or reflection spectrum ($\Delta \lambda$, $\Delta I$) or in a change of the scattering or reflection properties ($\Delta n$). Chromogenic materials usually are sensitive to only one specific stimulus thus defining several subclasses, such as thermochromic, photochromic, mechanochromic and electrochromic materials as illustrated in Figure 1 [1].

![Fig. 1: Chromogenic effects caused by external stimuli.](image-url)
Increasing importance gain those thermochromic systems which are generated using a function-by-design strategy which is based on physical or chemical interaction of no intrinsic thermochromic components [2].

Focusing on the topics (1) chromogenic plastic films by extrusion, (2) electrochromic panes and (3) piezochromic coating layers, the paper shows different development directions and active principles of chromogenic materials as well as the possibilities for controlling their specific optical properties. The wide application potential of these materials is illustrated on selected examples, such as packaging films with intrinsic temperature-controlled sensor properties (smart packaging), adaptive sun protection systems, electrochromic panes or pressure sensitive coatings.

2 Experimental

2.1 Chromogenic plastic films by extrusion

For the processing of the investigated chromogenic plastics, a flat film extrusion line of the Dr. Collin GmbH (Ebersberg, Germany) was employed. It consists of a single screw extruder E 25 M with L : D ratio of 25 X 25 which is completed by two extruders E 20 M with L : D ratio of 25 X 20. A feed block enables the extrusion of multilayer systems with up to 5 layers from three different polymer materials and with a width of 200 mm. Therewith it is possible to combine common plastics with thin functional layers by a co-extrusion process. The functional layer can be covered on the plastic film or it can be integrated within a multilayer array. More experimental details are given in chapter 3.1.

2.2 Electrochromic panes

The electrochromic pane is prepared by gluing two FTO-coated glasses of float glass with an acrylic adhesive tape along the edge. A composition consisting of various acrylates and methyl acrylates, a dry plasticizer, a binder, a conducting salt, as well as a photo starter along with the precursor of a conjugated organic polymer is stirred in the dark for 30 minutes. The mixture is filled into the cavity between the two FTO-panes. Afterward, the edge of the laminate is sealed with a two-component resin. Subsequently, the laminate is hardened by UV light exposure. By applying a low DC voltage, a transparent polymer film forms on the anodic FTO-layer that turns colored when the voltage is removed. The composite is decolorized by briefly applying (a few seconds) a predetermined DC voltage (OFF state), the same voltage of opposite polarity colors the pane again (ON state). A glass laminate produced in this way withstands a force of \( F_{\text{max}} = 11.1 \text{ kN} \) at the stamp pressure test based on DIN ISO 614. The switching time to reach the maximum color (transmission at Abs\(_{\text{max}} < 48\%\)) for a 300 mm x 300 mm sample is below 5 seconds with a switching current of 5 mA. The time for the discoloration is 8 seconds (transmission at Abs\(_{\text{max}} > 74\%\)).

2.3 Piezochromic coating layers

A basic preparation procedure of piezochromic films is given in [3]. The approach uses cholesteric liquid crystals, polymerizable cholesterics, a crosslinker and a photoinitiator forming a polymer network by UV photopolymerization. In the present study Cholesteryl [4-(6-acryloyloxy)-hexyloxy] benzoate (CAHB) was used as reactive mesogen. The specimen consists of a 90 µm piezochromic layer sandwiched between two layers of which at least one is transparent, and one is equipped with an aligning layer for planar orientation. The pressure sensitivity was estimated using a force gauge PCE-FM50 equipped with a planar tip of 50 mm\(^2\) area. The threshold of pressure sensitivity was related to the applied force which provokes a clear color change in the film.

3 Results and Discussion

3.1 Chromogenic plastic films by extrusion

Commercially available plastics are not chromogenic by themselves. In order to achieve chromogenic properties in plastic matrices, they need to be doped with specific
additives or chromogenic pigments. Especially chromogenic functionalized thermoplastics are of practical importance as they can be processed by extrusion techniques. Two examples of recent developments at the Fraunhofer IAP will be presented regarding a thermochromic plastic film as packaging material with intrinsic temperature control as well as thermotropic materials for adaptive sun protection films and coatings.

### 3.1.1 Thermochromic films by extrusion

Thermochromic packaging films with inherent temperature sensor function are the subject of intensive investigations at the Fraunhofer IAP. These films can indicate the interruption of the cool chain or a significant deviation from the allowed storage temperature of heat sensitive goods without further technical means by an explicit color change. They are a brilliant example for the constant efforts for smart packaging.

With respect to this, one approach comprises thermochromic leuco dye-developer-solvent systems exhibiting a pronounced supercooling behavior provoked by the balanced solvent components [4]. The so-called semi-permanent color changing materials lose their color above a predefined switching temperature. The pronounced supercooling behavior prevents a return of the color when the temperature has decreased, and the material stays colorless until an extended deep-freezing the color restores.

The principle is already commercially available in the form of microencapsulated composites. By embedding the composites into polymer matrices without encapsulating them, the Fraunhofer IAP obtained thermochromic materials with a semi-permanent color change. Hereto, a series of promising solvents were synthesized. They were combined with several leuco dyes and developers in polypropylene and polyethylene and were processed by extrusion to thin flat films. Thus, upon heating and cooling, they exhibit a pronounced temperature variance between a colored and a colorless state named as hysteresis (Figure 2). Up to now, hysteresis values up to 45 K could be achieved in the thermochromic plastic films. The work will be advanced to further develop this interesting approach in the field of smart packaging.

![Figure 2: Hysteresis loop of color intensity of a semi-permanent thermochromic composite in polypropylene obtained from absorbance values.](image)
3.1.2 Thermotropic materials by extrusion

The integration of thermotropic properties into extrudable plastics is of high economic relevance and enables the easy and efficient manufacture of adaptive sun protection films and multilayer sheets. These materials can be applied for the glazing of greenhouses and buildings, for roofs and for agricultural films.

For the manufacture of thermotropic polymers, the Fraunhofer IAP developed additives with temperature dependent refractive index which can be doped into thermoplastic polymers (PE, EVA, etc.) [5, 6]. At elevated temperature scattering centers with a diameter smaller than 1 μm are formed leading to an opacity of the material and to a strong increase of the reflection of the incident radiation (Figure 3). Therefore, thermotropic materials can be used for the adaptive shadowing of heat sensitive objects or as smart heat protection glass.

![Diagram of thermotropic materials](image)

Fig. 3: Active principle of thermotropic materials.

Former studies on different polyethylene grades yielded good results with thermotropic core-shell particles by extrusion to films at relatively low temperatures (120 °C – 160 °C) [7]. The thermotropic particles resisted the thermal and mechanical impact of the extrusion processes. Temperature-dependent changes of the normal-normal transmittance $\Delta T_{nn}$ of > 40 % could be achieved in these thermotropic PE films.

Now, the concept was transferred to ethylene-vinyl acetate copolymer (EVA), a plastic widely used in agricultural films. Different EVA grades (Elvax / Dupont) providing high optical transparency were combined with adapted thermotropic particles by extrusion at 130 °C – 140 °C. An additive concentration of only 3% was chosen. By variation of the temperature, the obtained thermotropic EVA films showed excellent changes in the normal-normal transmittance. Above the predefined switching temperature of 35 °C < T < 45 °C the transmittance of all samples decreases rapidly. Transparency changes of up to 36% were observed. Having the low additive concentration in mind the results could be considered to be very good.

3.2 Electrochromic panes

Electrochromic panes can be switched between different colored redox states by applying a specific voltage [8]. Classical electrochromic glasses are produced by vacuum deposition of metal oxides as tungsten oxide on a conducting glass substrate. The electrode material of choice is the low-cost fluorine-doped tin oxide (FTO). That layer provides the necessary surface conductivity but is still sufficiently transparent for the use on glass. The mentioned electrochromic compounds change their color by an electrochemical reaction with lithium ions from the conducting salt in a gel electrolyte. That conductive lightly cross-linked gel electrolyte is used to combine both panes to a laminate.
But not only inorganic metal oxides inherit electrochromic properties. Highly conjugated organic polymers can alter their color as well if they are changing between an oxidized and a neutral form [9]. Being mixed in a conductive matrix, those can be polymerized on a conductive substrate by the application of a respective voltage. Besides the simple manufacturing of the polymer-based electrochromic windows, the organic synthesis of the corresponding precursor materials offers, in general, the opportunities for a larger color variety in the so far blue dominated electrochromic panes market.

Electrochromic windows must be not only visually appealing but also mechanically extremely stable to be considered for the demanding application in architecture. Therefore, the monomeric precursors are blended with a specifically developed electrically conductive resin which is cured between two FTO-coated glasses by UV irradiation (Figure 4). That results in a window withstanding very high stresses and fulfilling the prerequisites, which apply to walkable or overhead glazing [10]. However, at the same time, the casting resin retains an excellent conductivity.

The electrochromic properties are obtained after the curing of the resin: By applying a voltage, the electrochromic layer is deposited on one of the transparent electrodes. A variation of the polymerization time can be used to individualize the switching intensity. The actual electrochromic switching takes place at a lower voltage of only a few volts. In addition, the power consumption is extremely low. Only 20 – 30 seconds pass until a 1.2 m² (~13 sqft) sized pane reaches the color maximum (Figure 5). The switching time is clearly below the 10 – 15 minutes that a WO₃ based window needs. Small electrochromic cells of less than 100 cm² already switch within 1 – 2 seconds. Thus, they are suitable for the use as a display element.

Fig. 4: Schematic representation of the production steps for an electrochromic resin-based pane.

Fig. 5: The 1.2 m² sized electrochromic pane exhibited at the Glasstec 2016.
3.3 Piezochromic coating layers

Advances in stimuli-responsive photonic polymer coatings were recently reviewed by Stumpel et al. [11]. This paper summarizes recent developments in polymer coatings with an intrinsic periodic structure which is changed by external stimuli, such as light, humidity, pH-value or temperature. Such coatings have a broad application potential as sensor layers (optical, humidity, chemical, biochemical, biomedical etc.).

A piezochromic polymer suitable for coatings and laminates was developed at Fraunhofer IAP [3]. It is based on cholesteric liquid crystals and reactive mesogens forming a polymer network by photopolymerization. Pressure-sensitive color changing properties in the single bar range could therewith be achieved. The piezochromic effect is based on changes in the periodic structure of the layer. The helical structure of the cholesteric liquid crystals is stabilized by an elastomeric polymer network obtained by photopolymerization defining the photonic and mechanical properties of the layer system. The periodicity of the helix structure satisfies Bragg’s law and thus leads to a selective reflection of incident light. Applying forces, the polymer stabilized cholesteric phase responds reversibly with a change in structural parameters, i.e. the reflecting color changes.

The initial reflection color, as well as the piezochromic sensitivity, can be adjusted by the ratio of reactive mesogen and cholesteric LC mixture (Figure 6).

Fig. 6: Optical impression and piezochromic properties of selected samples with different content of reactive mesogen CAHB.

A higher portion of reactive mesogen CAHB leads to the formation of a more compact polymer network and hence a responsiveness to higher pressures. As the structural periodicity is decreased the initial reflection color is shifted to smaller wavelengths.

Further adjustment of pressure sensitivity was obtained by the replacement of the monofunctional crosslinker by a bifunctional one. Relating to samples 1 - 3 in Figure 6, the piezochromic layers with a bifunctional crosslinker respond to higher pressures (1, 2 and 4 bar, respectively). All samples show a high long-term stability.

So far, the approach is suitable for coatings and laminates. A colorful responding system needs the formation of a highly ordered cholesteric polymer network. This is still a main challenge as well as the adaption of the approach to printable solutions, inks etc., which will remarkably increase the application potential.
4 Conclusion

Chromogenic polymers are materials with controllable optical properties. They exhibit color changes by external stimuli, such as light, temperature, mechanical forces or electric potential. Chromogenic polymers can also show transitions between a transparent and a scattering or a reflective state. The stimulated changes in optical properties of these materials offer a high flexibility in application for thin films and coatings. The broad application potential covers packaging films with intrinsic temperature-controlled sensor properties, adaptive sun protection systems, electrochromic panes or pressure sensitive coatings.

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References


Metallopolymers and non-stoichiometric nickel oxide: Towards neutral tint large-area electrochromic devices

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Abstract

Wet-chemical approaches were used to fabricate low haze (<2%) electrochromic (EC) thin films of different chemical nature, but compatible to each other in terms of coloration and electrochemical properties. A metallo-supramolecular polyelectrolyte (Fe-MEPE) film is shown to exhibit a large visible light transmittance change ($\Delta \tau_v$) of 54% when switched from the deep blue-violet Fe$^{2+}$ to the pale-green Fe$^{3+}$ state. On the other hand, a soft sol-gel peroxo-based approach was utilized to fabricate non-stoichiometric nickel oxide (Ni$_{1-x}$O) thin films on transparent conductive glass at low process temperature. Ni$_{1-x}$O, due to the Ni$^{2+}$/Ni$^{3+}$ redox couples present, shows an immediate electrochromic response with a $\Delta \tau_v$ of 44% when switched from the colorless Ni$^{2+}$ state to the grey-brown mixed valence compound. Proof-of-concept is given for a glass-based EC device combining Fe-MEPE and Ni$_{1-x}$O electrodes for the first time. The excellent EC performance is manifested in a $\Delta \tau_v$ of 47% and a contrast ratio (CR, 578 nm) of 32 for the full cell. The thin EC films presented can be deposited on conductive substrates including transparent conducting film (TCF) via spin-coating, dip-coating, or slot-die deposition. The viability of this approach for later industrial production is demonstrated by roll-to-roll (R2R) coating trials on polymer-based films.

Keywords: metallo-supramolecular polyelectrolyte, nickel oxide, neutral tint, large area electrochromic devices

1 Introduction

EC materials in thin film form exhibit optical transmittance modulation upon electrochemical oxidation and reduction.[1] In detail, charge carriers are injected in or extracted from the electrodes, thus producing redox states with different optical absorption characteristics. At the same time, cations or anions are inserted in or extracted from the electrolyte to provide charge compensation. A prominent and well-known anodically coloring EC material is nickel oxide, which has high potential for attaining neutral tint coloration, a sought after property of smart windows.[2] The color of nickel oxides is highly sensitive to the presence of higher valence states of nickel, even in traces.

Therefore, a variety of methods have been used to prepare anodically coloring EC nickel oxide films. The commonly used physical film deposition methods, e.g. sputtering or electron beam evaporation, involve high vacuum conditions and yield as-prepared films that may require pre-treatment before device assembly to obtain proper cell performance.[3] On the other hand, wet-chemical processes for colloidal EC materials are increasingly important due to the coming of plastic film-based EC devices employing polymeric EC films. Such materials are relatively easy to deposit via wet deposition techniques, enabling cheap mass production of flexible EC devices.

Both aspects are covered by the detailed studies of Mihelčič et al.[4,5,6] Here, the preparation and deposition of pre-prepared Ni$_{1-x}$O pigment particles leads to porous anodic EC pigment coatings allowing the easy insertion and extraction of small ions.[4] Moreover, this approach explores the deposition of Ni$_{1-x}$O on conductive films via wet-chemical deposition and subsequent heat-treatment at 150 °C. The as-prepared Ni$_{1-x}$O pigment coatings exhibited an immediate and strong EC effect when the pigment coatings were cycled in various protic and aprotic electrolytes, e.g., LiClO$_4$ in propylene carbonate (PC). In addition, non-stoichiometric Ni$_{1-x}$O films exhibit reasonable stability in non-aqueous Li-based
electrolytes.[2,7] The method is simple and easy to adapt for large-scale wet-chemical deposition, such as dip-coating, spraying, printing and R2R coating on appropriate substrates has been demonstrated in the EU-funded collaborative project EELICON.[8]

As a complimentary coloring and thoroughly investigated EC material metallo-supramolecular polyelectrolytes have been chosen.[9,10,11] The MEPE’s strong optical absorption in the visible range is due to a metal-to-ligand charge-transfer (MLCT) transition. Their optical properties can hence be modified by changing metal ions and ditopic ligands in the supramolecular assembly step, which makes them a very versatile EC material.[11,12,13] The Fe-MEPE chosen for this study consists of Fe(II) ions, bis(terpyridine) ligands and acetate (OAc−) counter ions and exhibits a reversible electrochromic effect due to the oxidation from Fe2+ (blue-violet) to Fe3+ (faint green) and vice versa. In recent literature, it has been shown that MEPE show high contrast ratios, short response times, high cycle stability and high coloration efficiencies.[9,10] In addition, this material can again be deposited via different wet-chemical techniques, e.g. layer-by-layer deposition or dip-coating.[14] A prior successful attempt to combine Fe-MEPE and a metal oxide, i.e., V2O5, for flexible EC devices was used to perform in operando x-ray absorption fine structure (XAFS) measurements to confirm that the octahedral coordination geometry in the Fe-MEPE material is not associated with any structural change during the switching process.[10]

In this work, wet-chemically prepared Fe-MEPE and non-stoichiometric Ni1−xO electrodes have been combined in an EC device for the first time. The Ni1−xO layers exhibit a significant modulation of their broad VIS-NIR absorption in non-aqueous Li-based electrolytes. On the other hand, Fe-MEPE shows exceptional coloration efficiency, a vivid color and high cycle stability. To the best of our knowledge, we report for the first time on an EC device of this configuration made completely by solution-based processes. It is noteworthy that the electrodes employed enable three distinct, individually addressable states in the EC device, i.e. (I) both electrodes are in their bright states, (II) Fe-MEPE is colored and Ni1−xO is still colorless, and (III) both electrodes are in their colored state.

2 Experimental

2.1 Materials and synthesis

All chemicals for the preparation of Ni1−xO powder and pigment coatings were purchased from Sigma-Aldrich and used without further purification.

2.2 Fe-MEPE synthesis and thin film preparation

4′,4′′′-(1,4-phenylene)bis(2,2′:6′,2′′-terpyridine) (tpy-ph-tpy) was synthesized according to the literature procedure given in ref. [15]. The Fe-MEPE was synthesized with a metal ion to ligand molar ratio of 1:1.[9,10] Fluorine-doped tin oxide (FTO) coated glass substrates (Pilkington, 14 Ω/sq) were rinsed in ethanol and dried with compressed air prior to dip-coating. Homogeneous thin films were prepared by means of a custom-made high-precision dip-coater (Fraunhofer ISC) from a 35 mmol MEPE solution at a withdrawal speed of 35 mm min−1. The Fe-MEPE films (~330 nm) were annealed at 60 °C for 24 h.

2.3 Preparation of Ni1−xO pigment dispersions and layers

The preparation of the Ni1−xO pigment dispersion was carried out according to a literature-known procedure. [4,5] In brief, the Ni1−xO pigment was synthesized via a sol–gel peroxoroute using a H2O2/urea mixture reacting with nickel(II) acetate powder. The obtained dried xerogel was thermal-treated at 400 °C for 24 h to obtain the non-stoichiometric Ni1−xO pigment.[4] Secondly, NiO:H2 dispersant and binder were prepared by precipitation of nickel(II) sulfate with sodium hypochlorite.[5,16] The precipitate was then rinsed in distilled water to remove sulfate anions and dried at 50 °C overnight. The pigment dispersion used consisted of 10 wt% of Ni1−xO pig-
ment dispersed in distilled water in the presence of dispersant, and, subsequently, was milled with zirconia beads.[4] The viscosity of the pigment dispersion was adjusted for a spin-coating process. Thin Ni$_{1-x}$O films were deposited with a rotation speed of 500 rpm for 5 s, followed by 1000 rpm for 1 min on FTO glass. For an increase of the film thickness the two-step spin-coating cycle was repeated several times. The deposition of thin Ni$_{1-x}$O films was accomplished by means of R2R slot-die coating on a COATEMA Smart Coater. Web speed was 0.1 m/min. Several running meters of Ni$_{1-x}$O coated on TCF 100 mm in width. The coatings were in-line heated for 6 min at 150 °C.

2.4 Preparation of glass-based EC devices

EC devices of the configuration glass/FTO/Fe-MEPE/gel electrolyte/Ni$_{1-x}$O/FTO/glass with an active area of 2 x 2 cm$^2$ were manufactured in an inertized glove box by the following procedure. The Fe-MEPE layer was prepared with an active area of 2 x 2 cm$^2$ surrounded by double-sided adhesive tape. A proprietary LiClO$_4$-containing gel electrolyte was prepared under dry conditions and doctor blade coated onto the active area (wet film thickness: 90 µm). The Ni$_{1-x}$O coated counter electrode was then aligned to match the electrolyte-coated working electrode and laminated on top. Adhesive Cu strips were used as bus bars.

2.5 Methods and instruments

The electrochemical properties of Ni$_{1-x}$O and Fe-MEPE films were determined in 1 M LiClO$_4$/PC electrolyte in a conventional three electrode set-up by means of standard electrochemical techniques such as CV. In brief, electrochemical characterization was carried out on the electrochromic half-cells, with metallic lithium as the counter and reference electrode. The Ni$_{1-x}$O and Fe-MEPE electrodes with an active area of 1 x 1 cm$^2$ were masked with tape and immersed in the electrolyte. Copper tape was attached to the FTO surface to maintain a good electrical contact. Electrochemical characterization was performed by means of a Solartron Multistat 1470E potentiostat/galvanostat. UV/Vis spectra were recorded with an Avantes AvaSpec-2048 standard fiber optic spectrometer combined with a balanced deuterium–halogen light source. Spectro-electrochemical measurements were performed in a custom-made two-electrode measurement cell with platinum as counter electrode and 1 M LiClO$_4$/PC as electrolyte.

3 Results and discussion

3.1 Cyclic voltammetry and EC properties of glass-based electrodes

Fig. 1 shows the CV results and optical transmittance spectra obtained for Fe-MEPE on FTO glass. The current-potential curves in the potential range 2.4 V to 4.2 V vs. Li/Li$^+$ were obtained at different scan rates (from 5 mV·s$^{-1}$ to 100 mV·s$^{-1}$). The peak potential for the oxidation of Fe$^{2+}$ to Fe$^{3+}$ occurs at 4.15 V vs. Li/Li$^+$, whereas the reduction takes place at 3.75 V vs. Li/Li$^+$. The oxidation and reduction of the Fe-MEPE film is accompanied by a marked color change from blue-violet to a virtually colorless faint green state. This effect is illustrated by the absorbance spectra in Fig. 1, where the MLCT band completely disappears at an applied voltage of around 2.0 V. The visible light transmittance change (Δτ$_{\text{vis}}$) value was calculated to be 54% and the CR (\(=\frac{\tau_0}{\tau_c}\)) where $\tau_0$ and $\tau_c$ are the transmittance in the bleached and colored state, respectively) to be 18 at 585 nm when switched between 0 V and 2 V.

The non-stoichiometric Ni$_{1-x}$O coated substrates were characterized accordingly. The current-potential curves in the potential range 2.4 V to 4.2 V vs. Li/Li$^+$ were measured at different scan rates (from 1 to 20 mV·s$^{-1}$) and are shown in Fig. 2. The anodic peak centered around 3.1 V vs. Li/Li$^+$ is assigned to the oxidation of Ni$^{2+}$ to Ni$^{3+}$ and de-intercalation of Li$^+$ ions. This process is accompanied by a reversible color change to a grey–brown tint. The cathodic peak centered around 3.2 V vs. Li/Li$^+$ is due to the reduction of
Ni$^{3+}$ to Ni$^{2+}$ and the simultaneous intercalation of Li$^+$ ions from the electrolyte into the Ni$_{1-x}$O structure. The reduction and intercalation of Li ions is accompanied by complete bleaching of the grey-brown colored films.

It is possible with a Ni$_{1-x}$O film to obtain a $\Delta \tau_v$ of 30% or 50% and a CR of 1.7 or 3.4 at 580 nm when switched between 0 V and 1.5 V or 2 V, respectively.

Fig. 1: Cyclic voltammogram (top) of Fe-MEPE films on FTO glass in 1 M LiClO$_4$ in PC with Li as reference and counter electrode at different scan rates. Absorbance spectra (center) of Fe-MEPE in 1 M LiClO$_4$ in PC with Pt as counter electrode and Ag/AgCl as reference electrode. Corresponding pictures (bottom) indicating the bleaching process.

Fig. 2: Cyclic voltammogram (top) of the as-prepared Ni$_{1-x}$O films on FTO glass in 1 M LiClO$_4$ in PC with Li as reference and counter electrode at different scan rates. Absorbance spectra (center) of the as-prepared Ni$_{1-x}$O in 1 M LiClO$_4$ in PC with Pt as counter electrode and Ag/AgCl as reference electrode. Corresponding pictures (bottom) indicating the coloring process.

The different chemical processes occurring in the nickel oxide film are difficult to describe in only one simple redox reaction in contrast to aqueous electrolytes, where the redox reaction
involves NiO and hydroxylated forms, such as Ni(OH)$_2$ and NiOOH.[2] Here, protons are the reversibly intercalated and de-intercalated species.[17] In the present study, a Li$^+$-containing non-aqueous electrolyte was used instead. The corresponding redox processes likely to take place in such electrolyte can be summarized by the following equations: [2,18,19]

\[ Ni_{1-x}O + y \cdot Li^+ + y \cdot e^- \rightarrow Li_yNi_{1-x}O \quad (1) \]

\[ Li_yNi_{1-x}O \rightleftharpoons Li_{y-2}Ni_{1-x}O + z \cdot Li^+ + z \cdot e^- \quad (2) \]

Equation (1) describes the initial bleaching process and equation (2) the reversible electrochromic reaction. Referring to the band structure, the color of the dark state is due to electron vacancies or holes around the nickel atoms, whereas the valence band is completely filled in the colorless state.[9]

The SEM image in Fig. 3 shows that the whole FTO surface (thickness: 420 nm) is well covered by smooth and compact nickel oxide with a thickness of approx. 1.25 µm obtained from the cross-cut image.

![SEM image of Ni$_{1-x}$O thin film on FTO glass](image)

Fig. 3: SEM images depicting the thickness (top) and the uniform coverage (bottom) of the Ni$_{1-x}$O thin films on FTO glass.

### 3.2 Electrochromic performance of the glass-based EC device

Electrochromic devices with the configuration glass/FTO/Fe-MEPE/electrolyte/Ni$_{1-x}$O-based-film/FTO/glass were fabricated to test the compatibility and efficiency of the Ni$_{1-x}$O electrodes (anodically coloring) in combination with Fe-MEPE electrodes (cathodically coloring). Fig. 4 shows that the blue-purple EC device (L$^*$ = 45.1, a$^*$ = 3.2, b$^*$ = -13.2) brightens up in ~10 s and can reversibly be colored in ~6 s. The absorbance spectra as well as the corresponding photographic images of the bright and colored states are depicted in Fig. 4.

![Absorbance spectra and photographic images](image)

Fig. 4: Switching time (top) for the EC device at cell potentials of 0 V and 1.5 V. Absorbance spectra (center) of the dark and bleached state of the as-prepared EC device with the corresponding pictures (bottom).
The as-prepared device only shows the absorption peak of Fe-MEPE, while the device brightens up completely (L* = 78.9, a* = -7.6, b* = 18.4) at an applied voltage of 1.5 V. When the device is switched to -2 V, both the Fe-MEPE and the Ni_{1-x}O are colored (L* = 34.2, a* = 13.2, b* = -6.0). The change from 8% (dark) or 14% (as-prepared) to 55% (bright) in visible transmittance results in Δτ values of 47% or 41% with CR of 13 or 32 at 578 nm, respectively. Comparing these values with examples from the literature makes it clear that the EC performance is outstanding. Fe-MEPE vs. metal oxides configuration are hardly investigated in literature. One example for a flexible EC device containing Fe-MEPE with similar absorbance at 587 nm and, hence, comparable capacity, and V_2O_5 can be found in ref. [10]. There, a Δτ value of 36% − from 22% (colored) to 58% (bleached) − was obtained. However, as opposed to the device of the present study, the bleached state was characterized by a pronounced yellow tint due to the optical absorption of the reduced vanadia. Further flexible devices utilizing Ni_{1-x}O as anodically coloring electrode show a ΔT_{480 nm} of up to 34% when n-TiO_2 is used as cathodically coloring material. A ΔT_{634 nm} of 25% was achieved with PEDOT or WO_3 as working electrodes. [5,6] The results of our study provide proof-of-concept that Ni_{1-x}O can also be used as EC active counter electrode for cathodically coloring Fe-MEPE layers with three distinct, individually addressable states − (I) both electrodes are in their bright states, (II) Fe-MEPE is colored and Ni_{1-x}O is still colorless, and (III) both electrodes are in their colored state. With respect to a future application in smart windows it seems possible to still increase the depth of coloration as in the current study a strong disbalance in the charge storage capacity of both EC materials was apparent (2.4 mC cm\(^{-2}\) for Fe-MEPE and 7.6 mC cm\(^{-2}\) for Ni_{1-x}O). Hence, higher coloration depth and a more neutral tint are expected to be attainable with thicker MEPE layers (i.e., higher capacity) and a broader range in cell voltage.

### 3.3 R2R coating

The above-mentioned approach describes the preparation of glass-based devices of small dimensions, but with promising properties towards the achievement of neutral tint smart windows. Fig. 5 demonstrates that the scale-up process from laboratory to pilot line production is straightforward, enabling a future device production by continuous coating and lamination techniques.[17] Here, both the nickel oxide and the MEPE films were processed via R2R slot-die deposition in coating trials on 125 mm wide TCF substrates.

Subsequently, the coated films were wound in rolls for easy storage and future processing (e.g., lamination, full cell assembly). The MEPE vs. Ni_{1-x}O system thus seems viable for future low-cost production of large-area electrochromic film devices.
4 Conclusion and outlook

In conclusion, we showed that the combination of easily processable Fe-MEPE and Ni$_{1-x}$O thin EC films on FTO-coated glass paves the way for a high-performance electrochromic system. The soft sol-gel peroxo-based approach with subsequent low-temperature heat treatment for the fabrication of Ni$_{1-x}$O thin coatings as well as the wet-chemical approach for the deposition of Fe-MEPE principally enable transferring the technology from glass-based to film-based, which is demonstrated by R2R coating trials. Further investigations will concern the color optimization towards neutral tints, optical contrast enhancement, and cycle stability validation for the MEPE/Ni$_{1-x}$O system.

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Trends and impacts of electro mobility and autonomous driving on plastic coatings.
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Abstract
E-mobility and autonomous driving are the two key trends disrupting the automotive industry. The concept and purpose of driving will change mostly in two ways: On one hand, the car will become a “driving living room” as there is no need any more to focus on the road or having input devices to drive the car. On the other hand, the importance of a car as a personal property might change as well: from the individual ownership of cars to a personal transportation service conducted by autonomous driving “people moving systems”. Both these trends demand new vehicle concepts and technologies. The plastic surfaces of the future need to fulfill more functional and aesthetic features to match with the changing demands from the disruptive trends. Plastic coatings will play a vital role in transforming plastic into smarter surfaces.

Keywords: E-mobility, Autonomous driving, plastic coatings, automotive interior

1 Plastics in the automotive industry
The primary future objective of car manufacturers is to make automobiles as economical as possible. Thus, plastics and composite components play a vital role in reducing fuel consumption and they offer great flexibilities to the designers. Apart from this, plastic materials will also have to offer additional functionalities driven by the future mobility aspects such as autonomous driving.

2 Impact on plastic coatings

Autonomous driving
Autonomous driving calls for additional smart and intelligent surfaces, such as “functionality on demand”, enabling a high level of personalization with high interior standards for the “driving living room”.

For example, a dashboard will have a huge decorative message display, pressure sensitive interfaces as alternatives to switches and knobs.

“People moving systems” require surfaces to be robust and more durable than ever before due to increasing usage. These surfaces also need to be antibacterial, odor free, stain resistant.

Independent of the application, coatings of these surfaces (including plastics) will become increasingly significant, not only for giving the ambient color and personalization but also to ensure the intended scratch resistance and extended durability and other functionalities.

However, the dashboards will be equipped with large displays, replacing important parts for plastic coatings, such as buttons and switches.

E-mobility
In e-mobility, weight reduction will remain the most important criterion for the car design. Therefore, the replacement of standard plastic or metal trim by lightweight alternatives such as natural fiber will gain importance. These natural fiber materials are either coated or laminated to increase their durability, performance and aesthetic appearance.

3 Current global automotive plastic coatings market
The current demand for automotive plastic coatings is about 100 kt. APAC region is the biggest consumer due to its large vehicle production (Fig. 1).
Exterior plastic coatings account for about 75% of the overall consumption. Bumpers account for 70% of the entire exterior coated surface in the exterior.

The major drivers for the demand of exterior coatings are (i) increasing automotive production, 2.5% (ii) replacing metal parts with plastics or other fiber-reinforced materials for weight reduction (impact of e-mobility).

Fenders and rear hatch show highest substitution potential for plastic parts and penetration rate of plastic roofs is also increasing.

This demand might be fueled by the increasing electric vehicle production.

The car category influences the penetration rate of coatings in the interior. In a low-end car, injection-molded plastic parts are often not coated. In a high-end car, more plastic parts are coated and higher share coated surface demand more coatings. The global automotive interior plastic coatings market will grow at a CAGR of 4% until 2022.

The increasing demand for more customized interiors will further drive the need for more coated plastic interiors. However, the exact impact of autonomous driving on the demand of coatings will only be clear after getting a more realistic picture about the design and features of future interior and the share of cars produced with “driving living rooms” to “people moving systems”.

4 Conclusion

Considering the different contradicting trends of electro-mobility and autonomous driving for the usage of plastics, it is currently hard to tell how this will affect the demand for plastic coatings in terms of volume. However, it is clear that plastic coatings will play a crucial role to satisfy customer demands generated by e-mobility and autonomous driving. Coating producers are becoming more and more value creators and have to offer a wider range of coatings to target the new demands and remain competitive.