ELECTROCHROMIC FOIL DEVICES
WITH VARIABLE OPTICAL TRANSMITTANCE

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ABSTRACT

Electrochromic (EC) device technology can be used for modulating the transmittance of visible light and solar radiation in windows in buildings as well as for other see-through applications. This paper emphasizes the great energy savings that can be achieved in the built environment, jointly with improved indoor comfort for the users of the building. Manufacturing aspects are considered with particular focus on potentially low-cost methods possible to implement with roll-to-roll technology. In particular the paper discusses recent work on foil-type devices embodying sputter deposited WO_3 and NiO-based films joined by a polymer electrolyte.

I. INTRODUCTION

Global warming is receiving world wide attention, and means to alleviate its harmful consequences are of the greatest urgency [1]. Major changes in energy technology will be necessary, which will impact global economy [2]. The changes must account for an increasing population, whose accumulation in mega-cities leads to “heat islands” which tend to enhance the warming [3].

The use of fossil fuel must be curtailed, which will influence the use of energy in industry, for transport, and in buildings. Particular attention on the built environment is natural considering the fact that this sector uses as much as 30 to 40 % of the primary energy in the world [4]. This energy is used predominantly for heating, cooling, ventilation, and lighting. In particular, the energy demand for air conditioning has grown very rapidly—by about 17 % per year—in the EU(15) [5], and already today electrically driven air conditioning dominates the peak power during the summer in parts of Europe as well as in the U.S.A.; in more extreme climates, the electrical peak power may be entirely dominated by air conditioning [6].

The increase in the energy expenditure for air conditioning is based on increasing demands for indoor comfort. Part of this lies in unwillingness to accept thermal discomfort due to too high or too low perceived temperatures; another reason is found in the wish to have good indoors-outdoors

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contact via large windows and glass façades. Large glazed areas tend to give cooling requirements, at least in commercial buildings in most parts of the world, but small windows lead to bad indoor comfort and hence poor job satisfaction with ensuing poor job performance. One way to improve the situation is to have building envelopes with variable throughput of visible light and solar energy, *i.e.*, "smart windows", as discussed further below. The same technology can be combined with light-guiding, which then opens possibilities to achieve energy efficient day-lighting via new concepts such as "light balancing" [7].

The energy savings inherent in the "smart windows" technology has been much discussed during the past several years. A simple "back-of-an-envelope" analysis illustrates this savings by way of an analogy: consider a surface with arbitrary orientation but facing the Sun; letting this surface be a "smart window" leads to a certain amount of saved energy, and letting it be covered with today's best solar cells for terrestrial applications leads to energy production of a magnitude that is the same as the savings in the case of a "smart window" [8]. More elaborate evaluations exist as well; the most detailed investigation so far was reported in recent work for the California Energy Commission [9,10].

The purpose of this paper is to discuss electrochromic (EC) device technology with particular emphasis on materials, production technology, and achievable optical modulation. It is a condensed version of a recently published conference report [11].

2. ELECTROCHROMIC DEVICE DESIGN AND MATERIALS

Several principles can be exploited to accomplish variable transmittance of visible light and solar energy [12,13]. Figure 1 illustrates the most widely investigated of these, which is based on electrochromism. The shown device comprises five superimposed layers on a transparent substrate, typically of glass or flexible polyester (PET) foil, or positioned between two such substrates in a laminate arrangement [14,15]. The resemblance to a thin-film battery is obvious. The outermost layers are transparent electrical conductors, typically of In_2O_3:Sn (*i.e.*, Indium Tin Oxide, ITO) [13]. One of these layers is coated with an EC film and the other is coated with an ion storage film with or without EC properties. The two films must consist of nanomaterials with well specified nanoporosities (analogously with the case of battery electrodes). A transparent ion conductor (electrolyte) is at the middle of the device and joins the EC and ion storage films. A voltage applied between the transparent electrodes leads to charge being transported between the EC and ion storage films, and the overall transparency T is then changed. A voltage pulse with opposite polarity—or, with suitable materials, short circuiting—makes the device regain its original properties. The optical modulation requires a DC voltage of 1 to 2 V. The charge insertion into the EC film(s) is balanced by electron inflow from the transparent electrode(s); these electrons can produce intervalency transitions, which is the basic reason for the optical absorption [15]. The devices do not display visible haze irrespectively of their absorption.

Regarding materials in the five-layer battery-type EC devices, the ITO can be replaced by ZnO:Al, SnO_2:F, or similar oxides, or, possibly, carbon nanotubes, if the availability and cost of indium turn out to be problematical [13]. The EC film is WO_3-based in almost all devices for window applications, whereas there are many possibilities for the counter electrode [14,15]. Among the latter, films based on IrO_2 and NiO have enjoyed much interest recently. IrO_2-based alternatives are inherently expensive, but good EC properties are maintained after dilution with cheaper Ta_2O_5

[16]. NiO-based films combine moderate cost with excellent optical properties; the transmittance can be boosted if the NiO is mixed with another oxide characterized by a wide band gap such as MgO or Al_2O_3 [17]. EC devices can use many different electrolytes, such as hydrous oxides exhibiting proton conduction and polymers with ion conduction due to added salts.

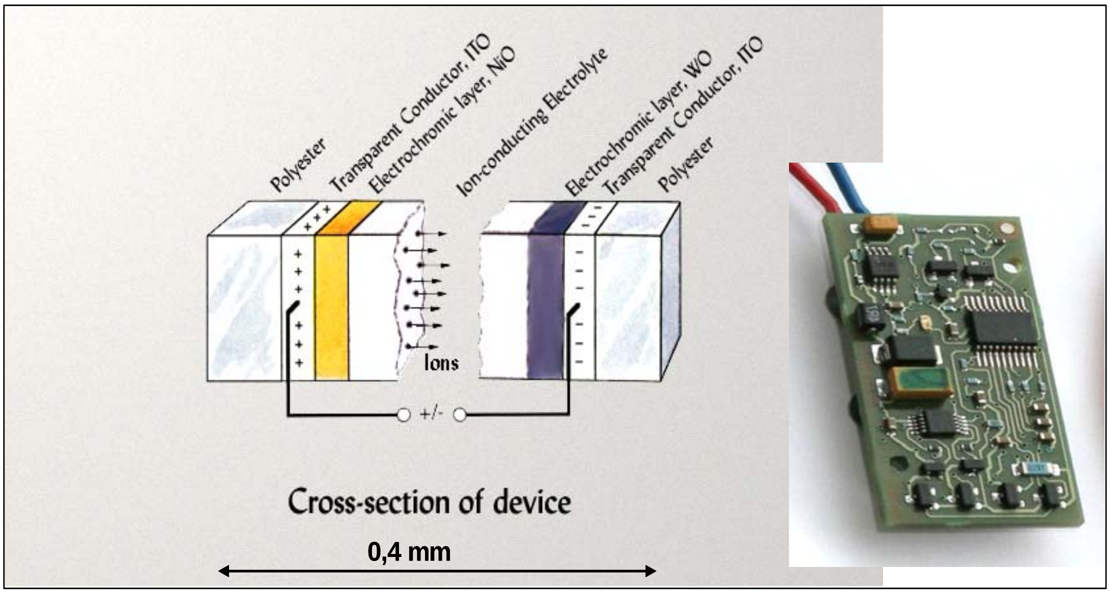

Fig. 1. Sketch of an EC foil-type device and the unit for supplying charge.

EC technology has been discussed for many years, but, generally speaking, the progress of this technology has been slow, which may be due to the fact that several non-standard procedures must be applied, as follows [18]:

(i) The ITO, or an analogous material, must combine excellent electrical conductivity with very low optical absorption, which requires special care for films on temperature sensitive substrates such as polymers [13]

(ii) The EC and counter electrode films must display well-specified nanoporosities over large areas, which calls for non-standard coating technologies

(iii) Viewing the EC device as a thin-film battery makes is evident that charge insertion/extraction and charge balancing are necessary and must be accomplished by properly controllable and industrially viable techniques, with gas treatment during or after film deposition being an interesting option [19]

(iv) The electrolyte must combine good ion conductivity with adhesiveness and high transparency for ultraviolet irradiation

(v) Long-term durability demands adequate strategies for voltage and current control during coloration/bleaching, just as it does for charging/discharging of batteries

All of these challenges can be successfully met, however, and EC technology finally may emerge as suitable for large-area, large-scale applications [20].

Film porosity on the nanoscale is required, as stressed in item (ii) above. Virtually any thin film technology may be capable of achieving the desired properties, though with more or less difficulty. Regarding sputtering [21], the deposition parameters should be confined to those giving “zone 1” films in the well known “Thornton diagram” [22] in Fig. 2 showing, schematically, what a sputter deposited film looks like in an electron microscope. Thin films for most applications are prepared under conditions such as the ones of the “transition zone” denoted T. Those films are compact and it is possible to minimize grain-boundary scattering of the conduction electrons in a metallic film. The transparent conducting ITO films in EC devices, for example, should be of this character. Nanocrystallinity and nanoporosity are found at higher pressure in the sputter plasma, such as in “zone 1”. It is then possible to have ion conduction in inter-columnar spaces, which is highly advantageous in EC films and in films for solid state ionics in general.

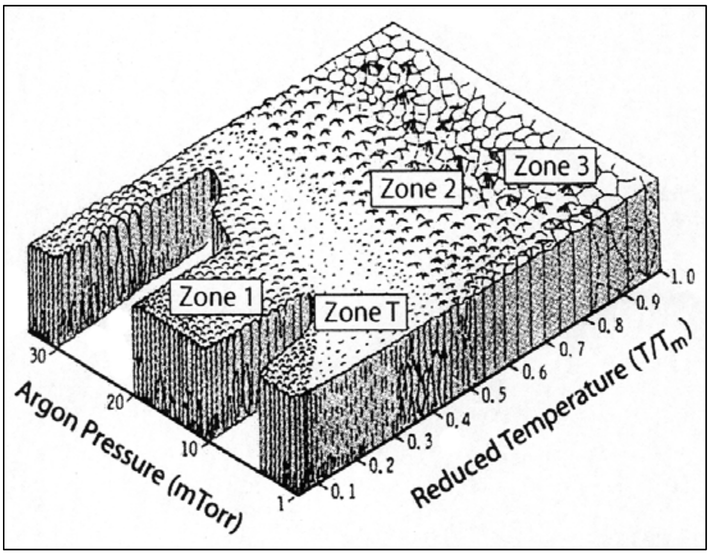

Fig. 2. “Thornton diagram” illustrating nanostructures of thin films prepared by sputtering at different argon pressures and substrate temperatures. The melting point of the material is denoted T_m. From Ref. 22.

3. DEVICE ASSEMBLY AND SOME PERFORMANCE DATA

EC devices were prepared by reactive DC magnetron sputtering onto 175-μm-thick PET foil from targets based on 99.95 % pure tungsten and nickel [15,23]. A target of $V_{0.07}Ni_{0.93}$ was used in many experiments; this made the target non-magnetic and hence convenient for magnetron sputtering. Deposition took place in $Ar + O_2 + H_2$ with optimized mixing ratio onto unheated substrates. The target-substrate distance typically was 20 and 25 cm, and the total gas pressure was in the 30 to 40 mTorr range. These conditions yield nanoporous films belonging to “zone 1” according to Fig. 2.

The device manufacturing has been industrialized in a manner consistent with the scheme in Fig. 3 [24]. Incoming PET foil is cut to pieces which are transferred to the sputter coater where a conducting pattern (“bus bars”), ITO films, and EC films are deposited. The WO_3 film is deposited in the presence of hydrogen so that it is charged and has a blue appearance. The NiO-based film is post-treated in ozone [19] and is then discharged and attains a brownish color. Coated foils of the two types are laminated together, supplied with electrical contacts, sealed, and tested. The particular devices produced in accordance with Fig. 3 were used in variable-tint visors for motorcycle helmets [25] as well as for window applications. Their dark-state appearance can be neutral gray.

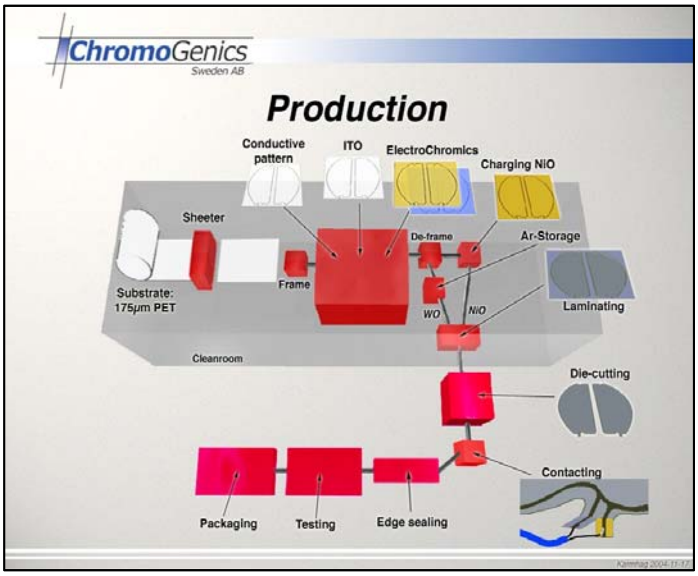

Fig.3. Production diagram for EC foil devices.

Powering the devices using units such as the one shown in the right-hand part of Fig. 1 led to ions being shuttled between the two EC films. The corresponding electrochemical "color reactions" can be represented as [15,26]

$$[\mathrm{Ni(OH)_2}]_{\mathrm{bleached}} \leftrightarrow [\mathrm{NiOOH} + \mathrm{H}^+ + e^-]_{\mathrm{colored}} \tag{1}$$

$$[\mathrm{NiO} + \mathrm{Ni(OH)_2}]_{\mathrm{bleached}} \leftrightarrow [\mathrm{Ni_2O_3} + 2\mathrm{H}^+ + 2e^-]_{\mathrm{colored}} \tag{2}$$

and

$$[\mathrm{WO_3} + \mathrm{H}^+ + e^-]_{\mathrm{bleached}} \leftrightarrow [\mathrm{HWO_3}]_{\mathrm{colored}}\ . \tag{3}$$

where e^- denotes electrons

The ensuing mid-luminous transmittance is illustrated in Fig. 4 for two consecutive color/bleach cycles adjusted so that the transmittance difference ΔT is 55 % [11]. The separation between points 1 and 2 corresponds to ~10 s and half of the transmittance span, the separation between points 1 and 3 corresponds to ~20 s and 90 % of the span, and the separation between 1 and 4 corresponds to 30 s and the full span in transmittance. Slower cycling would lead to a larger difference between the maximum and minimum transmittance.

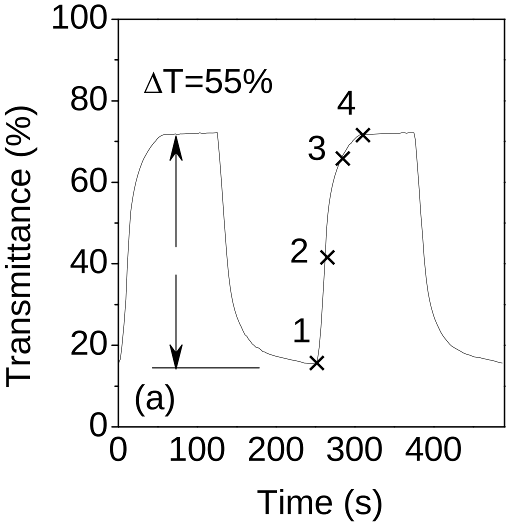

Fig 4. Mid-luminous transmittance for a 240-cm^2-size EC foil device showing the transmittance for two consecutive color/bleach cycles adjusted so that the transmittance difference ΔT is 55 %. From Ref. 11.

Figure 5 shows the evolution of the transmittance during the first 250 color/bleach cycles. The properties then could remain for tens of thousands of cycles. An actual visor in colored and bleached state can be seen in Fig. 6.

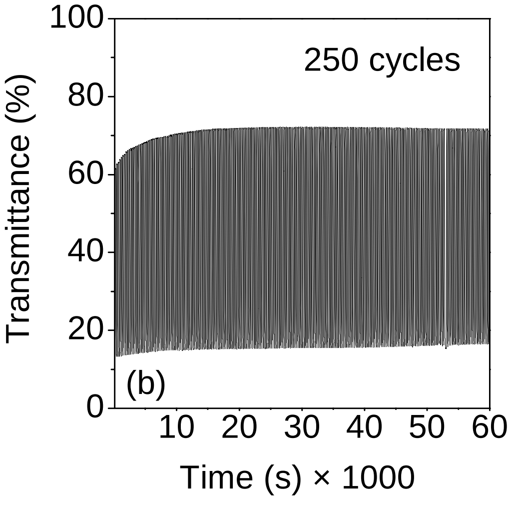

Fig 5. Mid-luminous transmittance for a 240-cm^2-size EC foil device showing the transmittance for 250 consecutive color/bleach cycles. From Ref. 11.

Fig. 6. Electrochromic visor for a motorcycle helmet in colored and bleached states.

The same technology was used in window prototypes, as illustrated in Fig. 7 where foils were positioned between glass panes. The upper two panels are colored and the lower two are bleached, and the haze-free nature of the EC foils is apparent. Up-scaling is currently under way in order to produce prototypes on a square meter scale.

Fig. 7. “Smart window” prototype with four 30 x 30 cm^2 panels.

4. SUMMARY AND SPECULATIONS

Electrochromic device technology, employed in the built environment, is emerging as one of the keys to combat the effects of global warming, and this novel technology may also serve as an example of the business opportunities ensuing from the challenges caused by the climate changes [2]. This paper introduced novel EC foil technology, which appears to offer possibilities to accomplish low-cost manufacturing of a material enabling energy savings jointly with comfort improvements in new and existing buildings. Manufacturing aspects and data from foil-type devices were presented, and the possibility to introduce the technology via consumer products—specifically visors for motorcycle helmets—was shown. In principle, roll-to-roll fabrication can be used.

Ending with some speculations, membrane architecture [27,28] may in the future be merged with EC foil technology in order to allow light-weight buildings with little embodied energy. ETFE is a well-proven polymer for such applications [29]. One can envisage huge membranes allowing the flow of visible light and solar energy to be controlled and optimized, thereby leading to resource-lean buildings. The possibilities offered by such membranes—although then based on glass technology—were pointed out more than fifty years ago by the great visionary Buckminster Fuller [30]. Perhaps this vision will come true thanks to electrochromics.

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