Solar Energy Materials & Solar Cells 93 (2009) 2032–2039

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Progress in chromogenics: New results for electrochromic and thermochromic materials and devices

C.G. Granqvist [a,*], P.C. Lansåker [a], N.R. Mlyuka [a,1], G.A. Niklasson [a], E. Avendaño [b]

[a] Department of Engineering Sciences, The Angstrom Laboratory, Uppsala University, PO Box 534, SE-75121 Uppsala, Sweden
[b] ChromoGenics AB, Märstagatan 4, SE-75323 Uppsala, Sweden

ARTICLE INFO

Article history:
Received 24 August 2008
Received in revised form
9 February 2009
Accepted 20 February 2009
Available online 26 March 2009

Keywords:
Chromogenics
Electrochromic
Thermochromic

ABSTRACT

Chromogenic device technology can be used to vary the throughput of visible light and solar energy for windows in buildings as well as for other see-through applications. The technologies can make use of a range of "chromic" materials – such as electrochromic, thermochromic, photochromic, etc – either by themselves or in combinations. The first part of this paper points at the great energy savings that can be achieved by use of chromogenic technologies applied in the built environment, and that these savings can be accomplished jointly with improved indoor comfort for the users of the building. Some recent data are presented on a foil-type electrochromic device incorporating tungsten oxide and nickel oxide. In particular, we consider the possibilities of controlling the near-infrared transmittance and optimize this property for specific climates. To that end we discuss Au-based transparent conductors for electrochromics as well as high-transmittance thermochromic multilayer films incorporating VO_2 and TiO_2.

1. Introduction

Global warming is receiving worldwide attention, and means to alleviate its harmful consequences are very much in focus [1]. Major changes in energy technology will be necessary, which will impact the global economy [2]. The changes must account for an increasing population, whose accumulation in mega-cities leads to "heat islands" that tend to enhance the warming [3,4].

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 30–40% of the primary energy in the world [5]. This energy is used predominantly for heating, cooling, ventilation, and lighting. In particular, the energy demand for cooling by air conditioning has grown very rapidly – by about 17% per year – in the EU(15) [6], and already today electrically driven air conditioning dominates the peak power during the summer in parts of Europe as well as in the USA; in a very hot climate, such as that of Kuwait, the electrical peak power may be entirely dominated by air conditioning [7]. It is important to note that energy savings in the built environment often conserve *both* energy and money [8], as elaborated in recent comprehensive studies [9,10].

The growth in the energy expenditure for air conditioning is based on increasing demands for indoor comfort. Part of this lies in persons' unwillingness to accept thermal discomfort due to too high or too low perceived temperatures; another reason is found in a wish to have good indoors–outdoors 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 too 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" [11].

"Smart windows" can make use of a range of chromogenic technologies [12,13], where the term "chromogenic" is used to indicate that the optical properties can be changed in response to an external stimulus. The main chromogenic technologies are electrochromic (EC) (depending on electrical voltage or charge), thermochromic (TC) (depending on temperature), photochromic (depending on ultraviolet irradiation), and gasochromic (depending on exposure to reducing or oxidizing gases). The present paper presents some new results related to electrochromic and thermochromic materials and devices.

Solar energy covers the wavelength $0.3<\lambda<3\,\mu m$. Part of this energy is visible light, which extends over $0.4<\lambda<0.7\,\mu m$ and includes about 50% of the solar energy. The ultraviolet, at $0.3<\lambda<0.4\,\mu m$, contains only a few percent of the solar energy,

* Corresponding author.
E-mail address: claes-goran.granqvist@angstrom.uu.se (C.G. Granqvist).
[1] Permanent address: Department of Physics, University of Dar es Salaam, PO Box 35063, Dar es Salaam, Tanzania.

0927-0248/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2009.02.026

whereas the near-infrared, at $0.7<\lambda<3\,\mu m$, carries close to 50% of the solar energy. Heat radiation, *i.e.*, the thermal infrared, lies in the $3<\lambda<50\,\mu m$ range. This present paper pays particular attention to the near-infrared transmittance of windows, which may be desirable for a building requiring heating but is unwanted for a building in need of cooling. As we will see in this paper, novel materials, such as gold-based transparent electrodes for EC devices as well as superimposed EC and TC layers, are of interest for achieving "smart windows" with optimized near-infrared properties and thereby optimized energy efficiency.

2. Some notes on the energy efficiency of chromogenic fenestration

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 an EC "smart window" with a large range between the dark (colored) and transparent (bleached) state 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 energy savings in the case of a "smart window" [14].

This analogy is highly simplified, though, and a more realistic analysis must also consider the role of electric lighting and many other aspects such as of the uses of the buildings under study. Such an analysis was done in some recent work for the California Energy Commission [15,16]. The summary of that report pointed at two items in particular: that EC windows could yield an annual reduction of the peak cooling load by 19–26% when controlled for solar heat gain, and that the energy for lighting could decrease by 48–67% when the windows were controlled for visual comfort. The comparison was made with today's best static fenestration technology as a baseline. Furthermore, and very importantly, the users of the building under consideration strongly preferred the EC windows since they led to diminished glare, lower reflections in computer screens, and less window luminance [16].

A recent study from the Madison Gas and Electric Company [17], from which Fig. 1 was taken, gives a very schematic illustration of the energies for cooling and for electric lighting with a number of chromogenics-based fenestration types. Not surprisingly, clear glass gives a comparatively small need for artificial lighting but is disadvantageous with regard to cooling energy. Tinted and reflecting glass diminishes the cooling energy but increases the demand for lighting. Chromogenic technology – especially the one based on electrochromics – is found to have strong advantages both for cooling energy and for electric lighting energy.

The energy savings potential inherent in chromogenic technologies is still poorly understood and a number of options are ready for further study. For example, combinations of chromogenic fenestration and light-guiding seem to open avenues towards very energy-efficient day-lighting via new concepts such as "light balancing" [18]. Also combinations of more than one chromogenic technology are virtually unexplored.

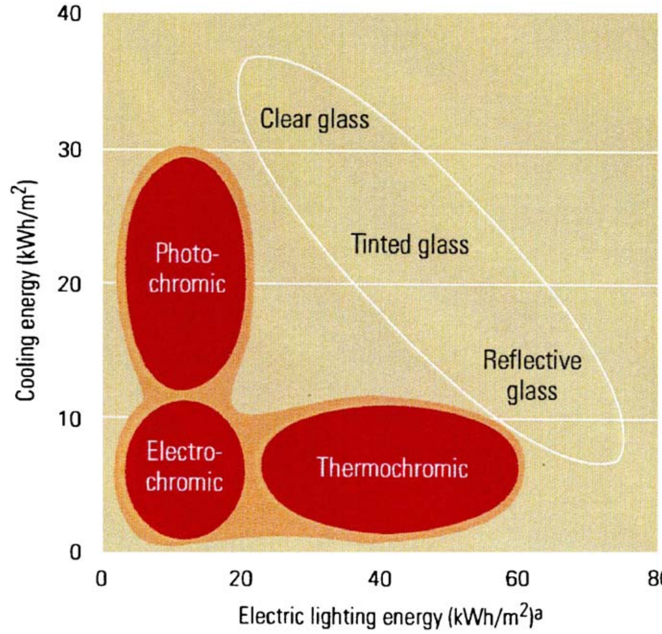

Fig. 1. Electric lighting energy and cooling energy for different types of fenestration. From Ref. [17].

3. Electrochromic devices

3.1. General device design and critical issues

Several principles can be utilized to achieve electrically controlled transmittance of visible light and solar energy [12,13,19]. Fig. 2 illustrates the most widely investigated of these; it 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 configuration [20,21]. The analogy 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) [19,22]. 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. 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 is then changed. A voltage 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 conductor(s); these electrons can produce intervalency transitions, which is the basic reason for the optical absorption [21]. The devices do not display visible haze irrespective of their absorption [23]. The latter feature distinguishes the EC five-layer design from other approaches to electrically variable transparency, such as the suspended particle devices [24].

We now consider the materials of interest for EC devices of the type shown in Fig. 2. Regarding the transparent conductors, ITO can be replaced by an alternative heavily doped oxide semiconductor such as ZnO:Al, ZnO:Ga, or SnO_2:F [19]. Metal-based coatings are possible too, as we return to below, and carbon-based alternatives (nanotubes [25] or graphenes [26]) may become of interest in the future. The EC film is WO_3-based in almost all devices for window applications, whereas there are many possibilities for the counter electrode [20,21]. 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 [27]. 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 [28]. EC devices can use many different electrolytes,