Solar Energy Materials and Solar Cells 185 (2018) 54–60

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

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

A new standard method to calculate electrochromic switching time

Sofiane Hassab[a], D. Eric Shen[b], Anna M. Österholm[b], Mathias Da Rocha[c], Giljoo Song[c], Yolanda Alesanco[d], Ana Viñuales[d], Aline Rougier[c], John R. Reynolds[b], Javier Padilla[a,*]

[a] Department of Applied Physics, ETSII, Technical University of Cartagena (UPCT), Cartagena 30202, Spain
[b] School of Chemistry and Biochemistry, School of Materials Science and Engineering, Center for Organic Photonics and Electronics (COPE), Georgia Tech Polymer Network (GTPN), Georgia Institute of Technology, Atlanta, GA 30332-0400, United States
[c] CNRS, Univ. Bordeaux, ICMCB, UMR 5026, F-33600 Pessac, France
[d] CIDETEC, Paseo Miramón 196, E-20014 Donostia-San Sebastián, Spain

ARTICLE INFO

Keywords:
Electrochromic switching time
Time constant
Coloration time
Bleaching time
Switching speed

ABSTRACT

The switching time is one of the key parameters used to assess the performance of an electrochromic material or device. In spite of its importance, there is currently no standard for how this parameter is defined, and as a result, it is difficult to compare switching time data between different research groups, and to quantify and assess reported improvements. We propose a standard method for reporting electrochromic switching times, based on straightforward experimental fittings resulting in an analytical expression that can directly correlate obtainable optical contrast values with their corresponding switching times. This analytical expression makes it possible to unambiguously define the performance of an electrochromic material or device using two parameters: a full-switch contrast and a time constant.

1. Introduction

Electrochromic (EC) materials are systems that reversibly change color in response to a redox reaction. These materials are of interest for a wide variety of applications, from on-demand tinting windows and goggles, to aesthetic signage and displays [1]. In all of these applications, it is important to define the time it takes to complete a full switch between two different optical states, as this parameter can determine their suitability for a specific EC application. Large area applications, such as architectural windows, do not require sub-second switching -whereas optical shutters and certain displays do. Currently, there is a lack of consensus about how switching time is defined. The conventional way of measuring switching time is to apply square-wave potential steps to the film or the device (Fig. 1a) while simultaneously monitoring the change in transmittance at a single wavelength (typically λ_{max}) (Fig. 1b). From this measurement, the time required to complete an arbitrarily chosen percentage of a full color switch is typically reported [2,3] (Fig. 1c). In some cases the current evolution instead of the transmittance has been taken into account to calculate the switching time [4,5].

The reason the time required to complete a full contrast switch is not typically reported is that the transmittance change as a function of time usually evolves in an exponential fashion, making it difficult to identify the precise time point that this occurs. Additionally, small transmittance variations are imperceptible to the human eye, and as a result the switching time for an EC material to complete 90 or 95% of its full contrast switch is often reported instead. However, many other values can be found in the literature, ranging from 50 [6], 60 [7], 66 [8], 70 [9], to 80% [10,11]. This makes it difficult to compare the switching times of different materials or devices tested under different experimental conditions. A description ofswitching time that is applicable to different EC materials while simultaneouslyoffering a simple means of measuring and describing this parameter is needed.

At least four aspects should be taken into account to meaningfully report switching time values:

First, from a practical point of view, reporting switching time values of an incomplete switch is inaccurate and confusing, as the actual time needed to obtain a full switch is in fact longer. The conventional approach of determining and reporting switching time presents an intrinsic disadvantage: reporting a switching time to an arbitrary Δ%T value does not contain any information about the additional time necessary for the EC material or device to obtain a full switch, as the transmittance vs. time response is not linear.

Second, the contrast corresponding to the switching time must be clearly reported as these two parameters are, by definition, linked to one another. Switching times reported to lower contrasts will inherently be faster and overestimate the film/device performance. Again, there is no information about the transmittance variations achievable for

* Corresponding author.
E-mail address: javier.padilla@upct.es (J. Padilla).

https://doi.org/10.1016/j.solmat.2018.04.031
Received 1 March 2018; Received in revised form 11 April 2018; Accepted 24 April 2018

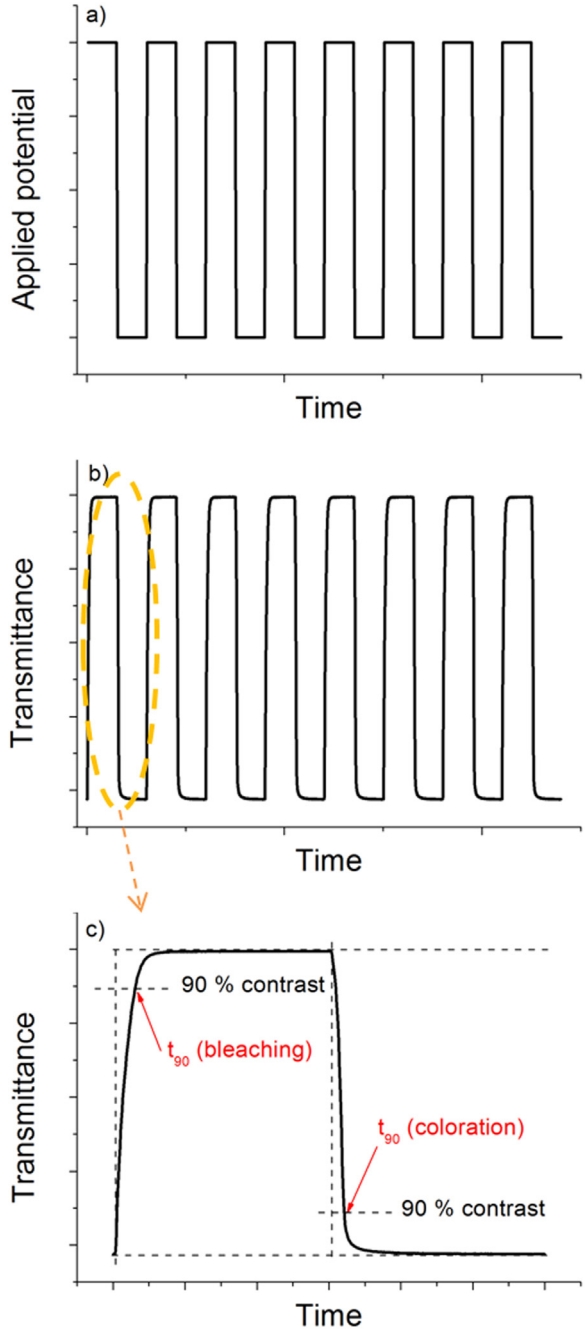

Fig. 1. Conventional procedure for reporting switching times. a) Square-wave potential steps with fixed pulse lengths. b) Corresponding transmittance evolution at a fixed wavelength. c) Switching time at an arbitrarily chosen percentage of a full switch (90% in this case), whether for bleaching or coloration.

shorter or longer pulse lengths or for films of varying optical density.

Third, and building off the previous point, different switching time values can be obtained for the same material if different transmittance variations are considered. This information would undoubtedly be useful for designing/optimizing any EC application (for instance, where a small compromise in contrast would be acceptable if the switching time can be noticeably improved, or to optimize the voltage pulse length to reduce energy consumption, etc.).

Finally, the switching time is significantly influenced by a variety of factors, whether intrinsic, such as film thickness or deposition technique used, or extrinsic, such as the counter electrode used, the choice of electrolyte, the distance between electrodes, electrode geometry, and the sheet resistance of the transparent conductor, just to name a few. Therefore, being able to accurately perform systematic comparisons between switching times obtained under different experimental conditions would certainly be useful.

The aim of this study is to provide a broadly accepted approach for the measurement of EC switching times, allowing results from various laboratories and on different materials or devices to be directly compared. We have identified an analytical expression, related to an exponential evolution, which describes the relationship between transmittance variation and pulse length necessary to obtain it, therefore constituting a practical operational tool to obtain switching time values and their corresponding contrasts. Importantly, this method can be applied to all EC materials and is demonstrated herein for metal oxides, viologens, and conjugated polymers. Furthermore, the method is applicable to both thin films and devices, expanding its practical value.

2. Results and discussion

Some of the issues linked to the present definition of switching time may be corrected or diminished if chronoabsorptometry responses could be directly fitted to a mathematical function. Diffusion controlled kinetic mechanisms, for instance, can generally be described by well-defined exponential decays. Unfortunately, descriptions of the electrochromic switching process are either usually more complex or not universally applicable for all materials [12]. Some attempts to mathematically describe switching times have been made in the past. Hu et al. [13] used a two-stage exponential function to describe the switching of polyaniline films; Faughnan et al. developed an expression for the switching time of oxides as a function of charge injected and other kinetically related parameters [14]. Green et al. considered a more complex function including diffusion coefficients [15]. Generally speaking, these various attempts show great complexity, in the form of extensive functions with many parameters involved, or are specifically developed for one kind of material (whether polymer or oxide) and cannot be extended to other material families.

A different approach consists of reporting electrochromic responses through a set of contrast vs. pulse length values. This has been explored in the past [16], although no analytical expression was proposed. With the aim of further exploring this relationship, we began with a case study taking a black-to-clear electrochromic random copolymer P[ProDOT$_m$-BTD] and evaluating the switching behavior of a set of 28 films with different redox capacities, i.e. charge-to-switch values (Table S1). The films were switched using square-wave potential steps (between 0.3 V vs. NHE where P[ProDOT$_m$-BTD] is colored and 1.3 V vs. NHE where P[ProDOT$_m$-BTD] is clear) of variable pulse lengths (30, 25, 20, 15, 10, 5, 3, and 1 s) and their transmittance evolution was obtained (Fig. 2a). The resulting transmittance vs. time curves showed that pulses of 10–15 s were nearly enough to attain a full switch of the corresponding films, where longer pulse lengths did not appreciably increase the contrast, while shorter pulses resulted in partial switches with decreasing contrast values. Plotting the contrast attained vs. the corresponding pulse length revealed a clear exponential growth evolution (Fig. 2b) that could be fitted to a function $f(t) = a(1-e^{-bt})$ showing excellent agreement with regards to the regression coefficients obtained for the whole set of films (Table S1). Fitting of the function results in two parameters, a and b, where the first represents the maximum achievable contrast value, corresponding to a full-switch of the EC material, and the second represents a time constant related to the speed at which the function evolves.

2.1. Proposed definition

Based on these initial results, the following procedure to obtain an analytical expression for the relationship between contrast and switching time for an electrochromic material can be proposed, opening a new path for defining switching time. Experimentally, the films or