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A NEW STANDARD METHOD TO CALCULATE ELECTROCHROMIC SWITCHING TIME

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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.

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

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].

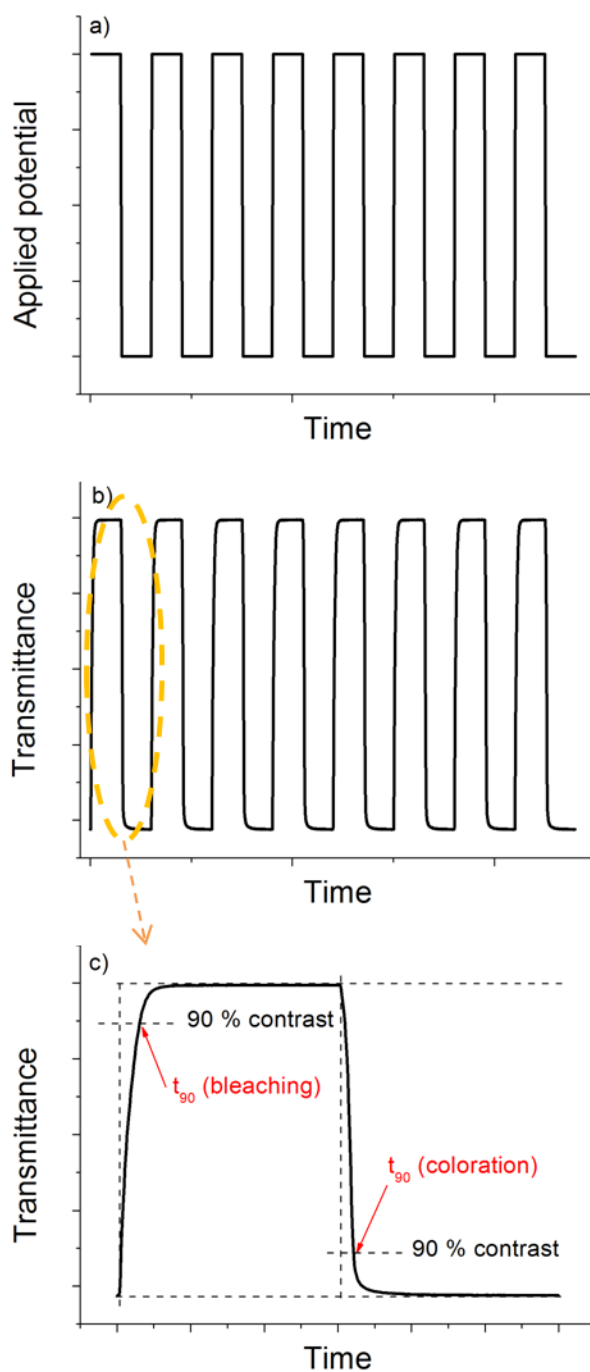


Figure 1. Conventional procedure for reporting switching times. a) Square-wave potential steps with fixed pulse lengths. b) Corresponding transmittance evolution at a fixed wavelength. c) Switching time at an arbitrarily chosen percentage of a full switch (90 % in this case), whether for bleaching or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

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 performed under different experimental conditions. A description of switching time simultaneously applicable to many different materials while offering a simple means of measuring and describing the 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 $\Delta\%T$ 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 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, making it of practical importance.

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, are generally accepted to promote well-defined exponential decays or rises. 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 begin 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.

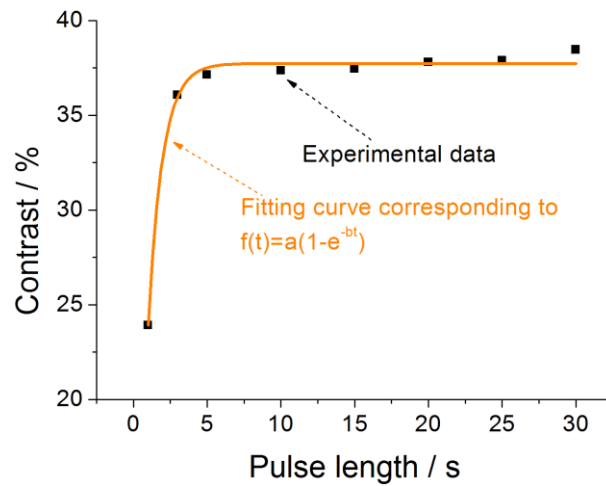


Figure 2. a) Chronoabsorptometric response of a polymer film P[ProDOT_m-BTD] (redox capacity 3.5 mC/cm²) using variable length potential pulses, 30, 25, 20, 15, 10, 5, 3, and 1 s, between 0.3 and 1.3 V vs. NHE. For each pulse length, potential steps are repeated five times (intervals at which each pulse length is applied are indicated in the figure). Inset figure shows the evolution for shorter pulse lengths (1, 3 and 5 s) b) Contrast attained vs. the corresponding pulse length. Orange line represents the fitting to an exponential growth function.

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 devices are switched using symmetrical potential steps (that is, same time applied for coloring and bleaching) of varying pulse lengths (Fig. 3a), and the transmittance variation at a desired wavelength (Fig.3b) is monitored. Films/devices are switched at each pulse length several times to assure a stable transmittance response and to obtain a statistically relevant value. Longer potential steps are applied to allow the film/device to reach stationary transmittance values in both states. Obtained contrast values as a function of pulse length can then be represented and fitted (Fig.3c) to the following exponential increase function:

$$\Delta T(t) = \Delta T_{max}(1 - e^{-\frac{t}{\tau}}) \quad (1)$$

Where ΔT_{max} represents the full-switch contrast obtained for long pulse lengths, and τ is the time constant. These two parameters contain all the necessary information to describe the relationship between an achievable contrast for a certain material or device, and the time necessary to obtain it.

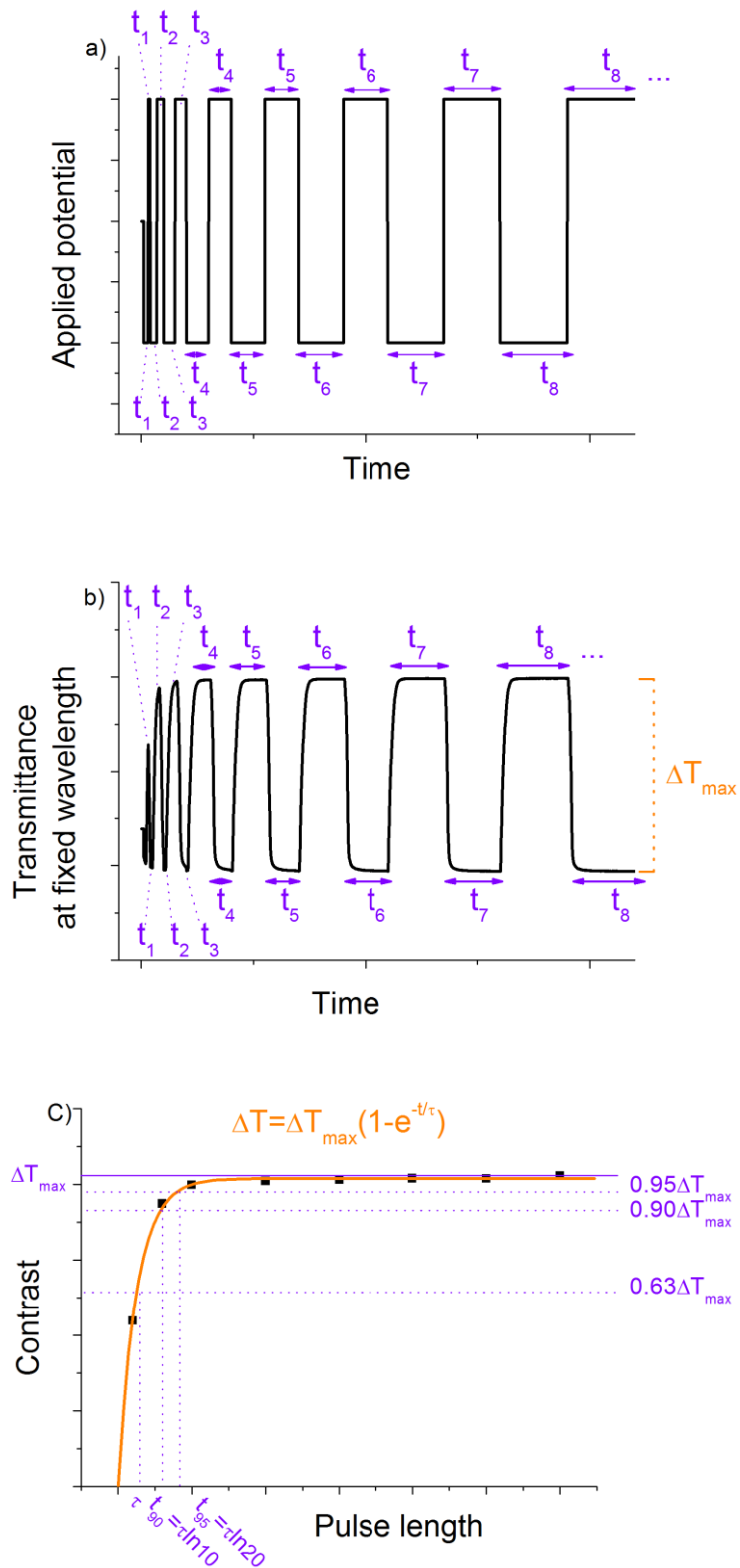


Figure 3. Symmetrical variable step time method: a) Square-wave potential steps with increasing pulse lengths ($t_1 < t_2 < t_3 < t_4 < t_5 < t_6 < t_7 < t_8, \dots$) b) Corresponding transmittance evolution at a fixed wavelength. c) Representation of the obtained contrast vs. pulse length values, and fitting to an exponential rise function.

The physical value of τ can be understood if we set the time t equal to the time constant τ . Then, the contrast obtained at a time τ will correspond to 0.63 of the full-switch contrast (i.e. 63% of a full transmittance variation), as is shown in Equation 2:

$$\Delta T(\tau) = \Delta T_{max} \left(1 - \frac{1}{e}\right) = 0.63\Delta T_{max} \quad (2)$$

Importantly however, we can easily obtain switching times for any other percentage of a full switch using the same equation. For a given fraction x of a full switch (where $0 < x < 1$), and denoting t_{100x} as the time necessary to obtain 100x % of a full transmittance change, this corresponds to the time necessary to reach $x\Delta T_{max}$. Therefore

$$\begin{aligned} x\Delta T_{max} &= \Delta T_{max} \left(1 - e^{-\frac{t_{100x}}{\tau}}\right) \\ x &= \left(1 - e^{-\frac{t_{100x}}{\tau}}\right) \\ e^{-\frac{t_{100x}}{\tau}} &= (1 - x) \\ e^{\frac{t_{100x}}{\tau}} &= \frac{1}{(1 - x)} \\ t_{100x} &= \tau \ln \frac{1}{(1-x)} = -\tau \ln (1 - x) \end{aligned} \quad (3)$$

From this, the following typically reported values, for example, can then be easily deduced:

$$t_{95} = \tau \ln 20 = 3\tau \quad (4)$$

$$t_{90} = \tau \ln 10 = 2.3\tau \quad (5)$$

This allows an easy direct comparison between different reported values, which constitutes one of the main advantages of this new definition of electrochromic switching time.

Experimental validation: Application to different EC materials

In order to assess the model's general applicability, the experimental procedure presented above was applied, not only to other conjugated electrochromic polymers, but also to transition metal oxides, and a viologen system. In addition to the random copolymer P[ProDOT_m-BTD], we also evaluated two other cathodically coloring EC polymers: ethylhexyloxy-functionalized poly(3,4-propylenedioxythiophene) (PProDOT-(CH₂OEtHx)₂ as another example of a soluble polymer as well as its electropolymerized and insoluble ethyl-functionalized analog PProDOT-Et₂ (see structures in Figure S1). Three commonly used inorganic EC materials WO₃, V₂O₅, and NiO were chosen to represent the metal oxide category, and

finally, 1,1'-diethyl-4,4'-bipyridinium dibromide (EtVio) was chosen as a representative of the viologen family. These materials were tested under a variety of experimental conditions, either in three-electrode configurations (polymers and metal oxides) or two-electrode device type configurations (polymers, metal oxides, and the viologen), and also using different electrolytes both in liquid or semisolid forms. Table S2 summarizes the main experimental conditions for each material or device type, including the previously mentioned set of 28 films of the polymer P[ProDOT_m-BTD]. The applied potential and pulse lengths were adjusted for each material to ensure that they would undergo a full contrast switch. In addition, to ensure that we would obtain a sufficient number of data points to accurately fit the contrast vs. pulse length data according to Equation 1, at least 8 different pulse lengths were used for each film or device.

Chronoabsorptometric responses were similar to that shown in figure 2a, where increasing contrast values were obtained as pulse length increased, reaching stationary values after a certain length for each film. Contrast versus pulse length values were extracted in each case and fitted to the function $\Delta T(t) = \Delta T_{max}(1 - e^{-\frac{t}{\tau}})$. From those fittings, values of ΔT_{max} , the contrast corresponding to a full switch, τ , the time constant, and the corresponding regression coefficient r^2 were obtained. Resulting values for these sets of films are shown in Tables S1, S3, and S4, (together with the corresponding t_{90} calculated from τ , as an example of the straightforward calculation of different switching time percentages). Excellent regression coefficients, with values well above 0.9, are shown for all materials, demonstrating the broad applicability of this model. Additionally, the goodness of fit of the regression coefficients was found to be independent of the time constant τ , proving that the fittings were equally valid for faster or slower films, as can be seen in Figs. 4a and 4b. It should be noted that the group of films studied cover a wide range of thicknesses, spanning from less than 100 nm to over 800 nm in the case of the metal oxides, or redox capacities from 1 to 8 mCcm⁻² (corresponding to approx. 300 nm to 900 nm) for the polymers.

Regarding contrast, experimentally measured maximum contrasts values showed excellent agreement with the fitted ones, as shown in Fig. 4c, where the linear regression of measured vs. fitted values shows an almost ideal slope of 1.04 and a regression coefficient of 0.99.

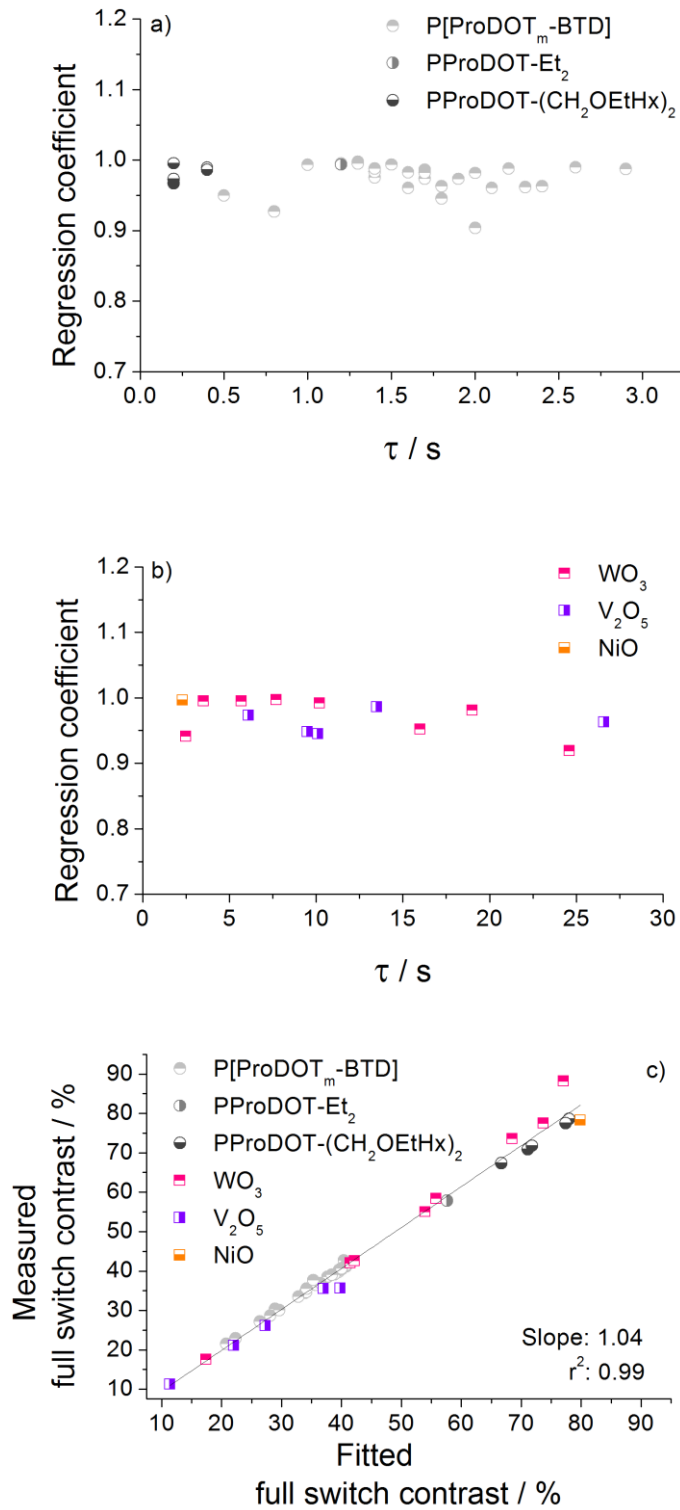


Figure 4. Regression coefficients for different EC films, as a function of the time constant τ a) for polymers P[ProDOT_m-BTD], PProDOT-Et₂ and PProDOT-(CH₂OEtHx)₂ and b) for oxides WO₃, V₂O₅ and NiO. c) Measured vs. fitted full-switch contrasts for different EC films.

Experimental validation: Application to EC devices

A set of devices was evaluated in order to demonstrate that the applicability of the proposed method expanded beyond films. Conjugated polymer devices and transition metal oxides devices were evaluated using liquid and/or semisolid electrolytes whereas the viologen system was evaluated using a gel electrolyte. The switching behavior in the polymer and metal oxide devices is fundamentally different from that of the viologen as the former two have the EC materials deposited as thin films on the conducting substrates while in the latter, the viologen and the counter ion species are dissolved in a gel. In the viologen device, the kinetic mechanism is expected to be limited by diffusion rate of the active species towards the electrodes whereas the switching reaction on the polymer or metal oxide devices can be limited by either ion diffusion in the electrolyte and through the EC film or by electron transfer in the EC film depending on the film thickness and the charge transfer resistance.

The two polymer devices incorporated a minimally color changing *N*-alkyl functionalized dioxypyrrole polymer (MCCP) [17] as the charge storage layer. In the PProDOT-(CH₂OEtHx)₂ devices, we ensured that the two cell halves were charge balanced, i.e. that the redox capacity of both PProDOT-(CH₂OEtHx)₂ and MCCP were equal. In P[ProDOT_m-BTD] devices, the redox capacity of P[ProDOT_m-BTD] was fixed at 4 mC/cm² for optimized contrast whereas MCCP redox capacity was varied. While MCCP's optical contribution to the device contrast is expected to be minimal, the higher redox capacity of thicker films may translate into slower switching films that could result in the P[ProDOT_m-BTD] and MCCP having very different switching times, which may influence the device switching. The PProDOT-(CH₂OEtHx)₂ device incorporated a solid, UV curable electrolyte whereas the P[ProDOT_m-BTD] based devices used a liquid electrolyte to further demonstrate that this method is applicable to different device architectures. Transition metal oxide-based devices were also tested, combining WO₃ and V₂O₅, both contributing to the final device contrast, with a semisolid electrolyte. A first device combined a slow WO₃ film (time constant of 19.0 s) with a faster V₂O₅ film (time constant of 6.1 s) while a second device consisted of a fast WO₃ film (time constant of 3.5 s) with a slower V₂O₅ film (time constant of 26.6 s). Finally, viologen-based devices were tested, combining EtVio in different concentrations as the color changing material and the complementary redox pair ferro/ferricyanide, in a PVA-borax based electrochromic gel, directly placed as a single layer between the two electrodes.

Table S5 summarizes the results for the maximum contrasts, the corresponding switching times, and the regression coefficients. Regarding contrast, experimentally measured full-switch contrast values showed excellent agreement with the fitted ones, as shown in Fig. 5a, where the linear regression of measured vs. fitted values shows an almost ideal slope of 1.05 and a regression coefficient of 0.99. Again, the majority of the fittings were found to be above 0.9, and practically independent of the time constant (Fig. 5b), with only a slightly lower *r*² values observed for some of the fastest PProDOT-(CH₂OEtHx)₂/MCCP devices (Fig 4.a and Table S3).

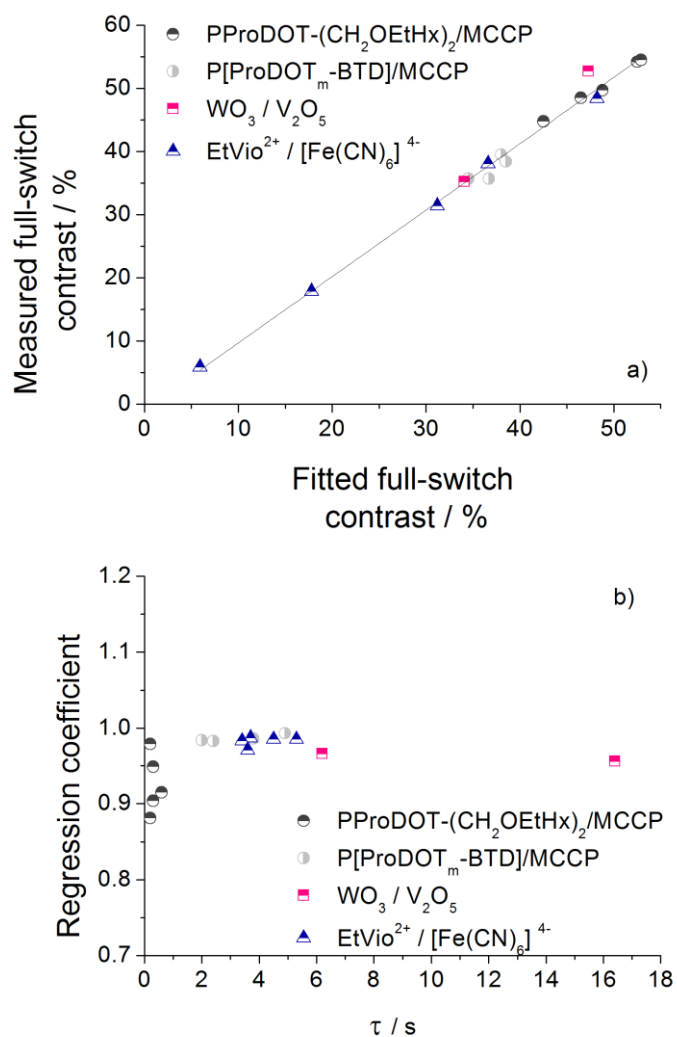


Figure 5. a) Measured vs. fitted full-switch contrasts for different EC devices, including polymer devices (PProDOT-(CH₂OEtHx)₂/MCCP and P[ProDOT_m-BTD_n]/MCCP), as well as transition metal oxide based devices (WO₃ / V₂O₅), and viologen based devices (EtVio²⁺ / [Fe(CN)₆]⁴⁻). b) Regression coefficients as a function of the time constant τ .

The good fittings obtained across all devices successfully demonstrate how our simple model is able to fit complex switching mechanisms involving two different redox active materials as well as an electrolyte. In addition to that, all devices are assembled by hand and across multiple research groups, which adds some sample-to-sample variation in terms of the distance between electrodes, electrode alignment, amount of electrolyte, etc. One of the main benefits of this method is its ability to accommodate complex exponential or non-exponential evolutions in the fitting while only needing to take into account a discrete set of points (initial and final transmittance values of each step). This is a significant advantage as it allows the inclusion of a great number of materials with different kinetic mechanisms.

Calculation of bleaching and coloration times

Some EC materials exhibit substantial differences in the bleaching and coloration kinetics, resulting in one of the process being faster than the other[18]. Nevertheless, symmetric pulse lengths are most frequently used when studying an EC material or device, and in spite of the different bleaching/coloration times, our proposed method can accurately describe and model a material's switching time using a single time constant. If, on the other hand, a detailed study of both the bleaching and coloration processes is needed, this method can be modified accordingly. In that case, asymmetrical pulse lengths where one of the processes (bleaching or coloration) is fixed and the other is varied can be used, as shown in Fig. 6, allowing to calculate bleaching and coloring response times separately.

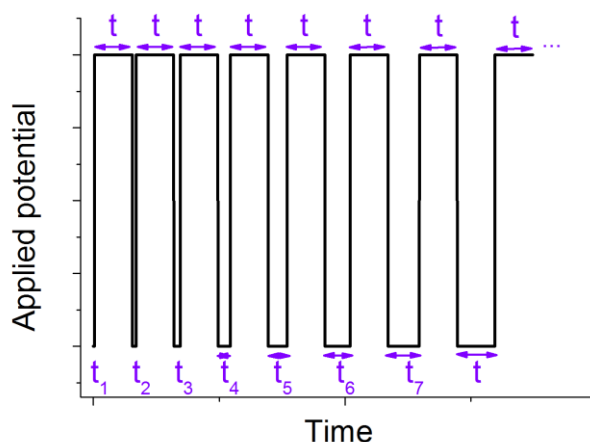


Figure 6. Asymmetrical variable pulse length method: Proposed modification in the applied potential profile for independent calculation of bleaching or coloring times. Cathodic or anodic pulse length is fixed (t) and the opposite steps are varied with increasing lengths ($t_1 < t_2 < t_3 < t_4 < t_5 < t_6 < t_7$, etc.).

In order to prove the validity of this modification, a number of films and devices were tested using this asymmetrical switching method. Results are summarized in Tables S6-S8. Table S6 shows the obtained fitted contrasts and the experimentally measured contrasts, for bleaching and coloration processes, where agreement between experimental and fitted values for both set of data is excellent. Overall, as shown in Table S7, fittings were satisfactory, with regression coefficients surpassing a 0.9 threshold in the majority of the cases, although slightly worse than those found applying the symmetrical switching method. No consistent trend was found, however, for those lower values. Samples based on PProDOT-(CH₂OEtHx)₂ are particularly relevant in this aspect, as the same films studied individually were later included and analyzed as part of a whole device. Fittings could be worse for either the coloration or the bleaching process but excellent for the symmetrical switching time (PProDOT-(CH₂OEtHx)₂ films of 2.0, 2.3 or 3.4 mCcm⁻²) or the opposite (PProDOT-(CH₂OEtHx)₂/MCCP device of 1.18 mCcm⁻²). Finally, first three data columns of table S8 shows the switching times calculated via symmetrical switching method, together with the time values obtained for coloration and bleaching processes calculated independently using the asymmetrical switching method. Differences in coloring and bleaching times were more pronounced for viologen devices and

metal oxides, and less perceivable for the studied polymers, especially when the values fell below the sub-second regime. Comparing those values with the previously obtained switching time values, it would be reasonable to assume that the values obtained during symmetrical switching should be closer to the slower process, be that coloration or bleaching. This seems to be the case for the viologen device, and the first oxide device, but when the switching time values fall close to the second or sub-second regime, distinction between the different methods is more complicated. Overall, for the faster samples, it can be said that all values fall in similar ranges, considering that accuracy beyond a tenth of a second is not reported in electrochromic studies. Researchers dealing with sub-second, i.e. video-rate targeted applications or beyond, are encouraged to pay special attention to the experimental setup (data acquisition rate, data precision) as subtle variations in the experimental data may result in significant deviations in the switching times obtained due to the exponential nature of the fitting function. Finally, it is noteworthy to mention the WO_3/V_2O_5 device (corresponding to 3.6/33.1 $mCcm^{-2}$, respectively) where switching time (obtained with the symmetrical method) differs substantially from coloration or bleaching times (obtained with the asymmetrical method). This sample was specifically included as significant electrochemical degradation (which reflects into lower contrast values) was observed between the firstly applied symmetrical method, and the afterwards obtained values from the asymmetrical method (Fig. S2). Researchers are therefore strongly encouraged to confirm the optoelectrochemical stability of the material/device during the experiment to obtain reliable values.

Comparison of switching time values obtained by different methods

Establishing a tool for proper and accurate comparison of switching times is the main objective of this study and two relevant questions arise: first, how do the coloring and bleaching times obtained with the new proposed method compare with the values obtained with the conventional method (i.e. as described in fig. 1). Second, how can a reliable comparison be made between values obtained in the past?

To assess the first question, conventional t_{90} values were obtained for a number of films and devices (the same set used in the previous section). As coloring and bleaching times are reported independently in the conventional method, for this comparison we used those values obtained by our modified, asymmetrical switching time procedure. The obtained values are shown in the last four columns of table S8 where there is an excellent agreement between our asymmetric switching speed methodology and the conventional methodology across a range of different materials, devices and architectures, and where slight differences can be attributed to the different approaches and calculations involved in the two experiments.

As for the second question, how to compare switching times obtained for different percentages of full transmittance variations, this comparison is not possible to make as long as dependence between contrast and switching time is not known. Some kind of analytical expression must be assumed to perform that comparison. We propose the use of the time constant (which implicitly assumes an exponential decay or rise for the chronoabsorptometry curves) so that a comparison can be made by back-calculating equations (3),(4) and (5) (i.e., if

a conventionally reported t_{90} value is known, the corresponding τ would be $\tau = \frac{t_{90}}{\ln 10}$, or if a t_{95} value is known, the corresponding τ would be $\tau = \frac{t_{95}}{\ln 20}$. A relationship between two switching times obtained to different contrast values can be generally expressed as follows: by x and y fractions lower than 1 ($0 < x, y < 1$), and denoting t_{100x} and t_{100y} the time necessary to obtain 100% or 100% of a full transmittance change, they can be expressed, according to equation (3), as

$$t_{100x} = \tau \ln \frac{1}{(1-x)} = -\tau \ln (1-x) \quad (6)$$

$$t_{100y} = \tau \ln \frac{1}{(1-y)} = -\tau \ln (1-y) \quad (7)$$

Solving for τ in any of the expressions and substituting in the other, the following expression can be readily obtained

$$t_{100x} = t_{100y} \frac{\ln (1-x)}{\ln (1-y)} \quad (8)$$

In either case, whether the new proposed method is used to switch an EC material or device, the time constant allows for direct comparisons between previously reported values where the switching times have been measured and calculated via conventional means, therefore setting up a bridge between the vast set of previously reported data and the new proposed way of reporting switching times.

4. Conclusions

In an effort to unify the many ways in which switching speeds have been defined in the electrochromic literature, we have proposed an experimental method that entails applying a series of symmetrical potential steps of variable pulse lengths, in which the longest one allows the material to reach a stationary full-switch contrast value. From this experiment, we have demonstrated the ability to extract an exponential function that correlates contrast with the time needed to obtain it. The key advancement of this method is that it allows extracting a characteristic time constant describing the exponential evolution, which allows for easy comparison between different percentage values, for readily calculating the time required to achieve different contrast values, and for deriving the time to reach various contrasts from literature values, assuming that the full-switch contrast is also reported.

We have experimentally demonstrated the applicability of this method for some of the most common electrochromic materials – conjugated polymers, metal oxides, and viologens – under a variety of experimental conditions, different electrolyte systems, and reproduced by several research groups. The switching times of any these materials could be precisely obtained by the exponential function, in spite of the differences in the ways in which they perform. Furthermore, the equations developed here were found to extend to electrochromic devices, despite the fact that device switching requires both an electrochromic and a charge storage material undergoing redox changes simultaneously.

We also demonstrate that our methodology not only applies to switching electrochromic materials in a symmetric fashion (i.e. equal pulse durations for oxidation and reduction) but also for asymmetrical potential steps in which one of the switching processes (coloring or bleaching) time is fixed and the other is varied. The simplicity of the proposed methodology allows for switching data to be directly compared between different EC materials, between data collected by different research groups, as well as with previously published data without drastically changing the experimental method.

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