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Process controlled performance for soluble electrochromic polymers

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ABSTRACT

We present a method that can be used to quantify and optimize the performance of electrochromic polymers and evaluate how the choice of coating method affects the film characteristics. The mathematical approach, together with a standard experimental procedure to perform it, is described. This method can be applicable to any electrochromic material and deposition technique with the only requirement being that the Beer–Lambert law is followed. Three common (and industrially applicable) coating techniques (namely spray, blade and spin coating), together with three solution processable electrochromic polymers (ECP-Magenta, ECP-Black and ECP-Cyan), were used in the study to illustrate the feasibility of this method. For all the evaluated polymers, the choice of deposition method had a direct effect on the maximum achievable contrast. Spin coated films tended to show the highest contrasts, closely followed by blade coated films and finally spray coated films. When explaining those differences we showed that coloration efficiency, widely used as an electrochromic quality parameter, is not directly related to achievable contrast values. Instead, we have proposed the volumetric redox density. It has been found that higher values of this magnitude translate into higher achievable contrasts.

1. Introduction

Continuous advances in the processability of conjugated electroactive polymers [1–11] have brought the possibility of mass producing devices, by means of solution and roll-to-roll techniques, closer. Considerations including process simplicity, speed of production or material consumption will play an important role in the final choice of deposition technique. One critical parameter that must be understood and quantified is how the active film deposition technique controls the performance of the resulting materials and devices. Developing an understanding of polymer structure, processing solution and deposition method inter-relationships will impact the fields of organic solar cells, field effect transistors, light emitting diodes, and, in the case addressed here, electrochromic devices.

Common magnitudes that define the performance of an electrochromic device include optical contrast, color change, switching speed, and the required voltage to power the device, along with long-term switching and environmental stability. Depending on the desired application, some of these variables prove to be more important (switching speed may be necessary for antiglare rearview mirrors while less relevant for architectural windows, for instance) but generally speaking, optical contrast is an inherent and necessary magnitude for any electrochromic device. In the extreme, with an absence of contrast, (defined as a change in the transmittance of the material, i.e. color) we could not properly talk about a ny electrochromic effect. Accordingly, a substantial portion of the scientific efforts in the electrochromic community are concerned with improving the optical contrast of electrochromic materials and devices.

There have been many advances in the contrast improvement of electrochromic polymer (ECP) films, mainly through synthetic efforts where the focus has been the structure of the main chain repeat unit [12-15], but also through less common approaches such as incorporation of viologens [16,17] or nanotemplate deposition [18,19] to name a few. Examining this field in general, one perceives a gap in applying a systematic method to quantify the corresponding improvements in electrochromic performance. When reporting contrast values, often just one film or a minimal set of films (frequently just the best experimentally obtained results on a trial and error basis) are reported. Optical performance of films synthesized or deposited using similar experimental conditions, but with different characteristics (different film thicknesses, for instance) are rarely reported and typically the relationship between these magnitudes is not discussed. A systematic method to quantify the contrast evolution of an electrochromic

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material as a function of a given variable has been proposed by Lim et al. [20] and further developed by Padilla et al. [21]. This method allows for quantification of the maximum contrast achievable and experimental conditions needed to obtain it for a given deposition technique, therefore avoiding the trial and error path. As a result, this method can be used to compare the electrochromic performance of a given material deposited under different conditions.

In this study, the value of this method is shown by comparing three common coating techniques used for preparing electrochromic polymer films, namely, spray coating, blade coating and spin coating, and showing how they can affect optical and electrochemical properties. This group of coating techniques constitutes a representative set of solution-based, industrially applicable fabrication processes [22]. Other deposition techniques, specifically electropolymerization, which are less likely to be easily adapted to large scale production, have been previously explored using this method [20,21]. Due to the different deposition and film-formation mechanisms present in each technique [23], variations in the appearance of the films are expected. During spin coating there is a radial uniform distribution of the material and fast evaporation of the solvent due to rotational forces. Blade coating, on the other hand, starts with a longitudinal uniform distribution followed by slower evaporation rates. Spray-coating normally has a much faster drying time, starting with ejected droplets that impact the substrate from above and then coalesce. Obviously, the variables that play an important role in the film quality differ substantially for each technique. For example, the morphology of spray-coated films is affected by the spray gun pressure and the nozzle–substrate distance. In blade coating, coating speed and blade gap, for instance, can be varied, while in spin coating several parameters can be adjusted such as e.g. rotational speed and spin time. With such diversity, this set of coating techniques appears to be an appropriate initial test bench with which to study their possible influence on the electrochromic performance of a material.

We chose to evaluate the effect of coating technique on the electrochromic performance of three solution processable polymers, namely ECP-Magenta [5,6], ECP-Black [24,25] and ECP-Cyan [26,27]. As with the coating techniques, diversity between the chosen polymers was pursued, in order to obtain as broad and general results as possible. These three polymers differ not only in color, but also their repeat unit structures are representative of different strategies used for contrast and color tuning [28]. ECP-Magenta represents an all-donor homopolymer of alkoxy-functionalized 3,4-propylenedioxythiophene (ProDOT). ECP-Cyan is an alternating donor–acceptor (D–A) polymer consisting of ProDOT and benzothiadiazole (BTD) units and ECP-Black is a broadly absorbing random D–A polymer (ProDOT and BTD units). Of these structures, ECP-Black has the lowest optical contrast and the ability to enhance the contrast through appropriate choice of coating method would be advantageous as it provides a route much easier than designing and synthesizing new and complex D–A polymers.

Here, we present a generally applicable, straight-forward experimental method to evaluate and optimize the electrochromic performance of any electrochromic material. Being a quantitative and predictive optimization tool, it would undoubtedly be helpful as a standard characterization method for the electrochromic community.

2. Theoretical basis

The optical characteristics of electrochromic materials are related to physical or chemical properties. The Beer–Lambert law states a linear relationship between absorbance (A), concentration of light absorbing species and optical pathlength (or thickness). The optical contrast of an electrochromic material is defined as the difference between two transmittance values (usually bleached and colored), where transmittance is, by definition, exponentially related to absorbance ($\%T = 10^{(2-A)}$ or equivalently $\%T = 100e^{-2.303A}$). As a result, optical contrast can be expressed as a subtraction of two exponential decay functions. The basis of this proposed method lies in the fact that expressed this way, the contrast function has a maximum that can be calculated. The maximum is situated at the point where the first derivative of the function is zero. Detailed calculations and development of the adequate nomenclature have been reported before [21], but the general mathematical results are as follows:

$$\Delta y(x) = 100(e^{-cx} - e^{-dx}) \tag{1}$$

$$x_{max} = \frac{\ln\left(\frac{d}{c}\right)}{d-c} \tag{2}$$

$$\Delta y_{max} = 100(e^{-cx_{max}} - e^{-dx_{max}}) \tag{3}$$

where $\Delta y(x)$ is a function defined as the subtraction of two exponential decays, and c and d are the decay coefficients, that are constant values.

Based on these mathematical relationships, anytime we experimentally find an exponential decay relationship between the transmittance values of different electrochromic films and corresponding deposition magnitudes (thickness, for instance), we will be able to describe the contrast function using Eq. (1). This allows for calculation of the point where the function has its maximum Eq. (2) and then to correlate that maximum to the corresponding deposition magnitude (e.g. film thickness). Substituting that into Eq. (3) yields the maximum contrast value. This allows for determination of the film thickness or redox capacity that will provide the best optical performance for a given electrochromic material and deposition conditions.

A qualitative description of the steps included in the method can be seen in Fig. 1. The absorbance of different films in their bleached and colored states is measured and plotted as a function of the desired optimization magnitude (for instance, film thickness or redox capacity) (Fig. 1a). Each pair of vertically aligned points represents a different film. If linear relationships are found, transmittance values ($\%T$) can be represented as exponential decays (Fig. 1b). When representing the subtraction of these two functions (Fig. 1c), a maximum can be clearly identified and quantified, and therefore directly correlated to a film thickness, redox capacity, or other film characteristic.

This method is not restricted to just the optimization magnitudes discussed here: it can be used as long as an exponential decay of transmittance caused by another experimental magnitude is found (this is equivalent to finding a linear relation between absorbance and those magnitudes). This method has been previously applied to optimize the contrast in terms of number of polymerization cycles [20] and redox capacity [21]. Here, in addition to redox capacity, we have also optimized the electrochromic performance of the studied materials as a function of film thickness.

3. Experimental

3.1. Materials and equipment

ECP-Black (M_n: 10 kDa, PDI: 1.6) was obtained by Stille polymerization, according to previously reported procedure [25]. ECP-Cyan