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Conjugated Polymers for Photo-electrochromic Devices

Buket Bezgin Carbas[1,2*]

[1]*Karamanoglu Mehmetbey University, Faculty of Engineering, Department of Energy Systems Engineering, Karaman*
[2]*Karamanoglu Mehmetbey University, Faculty of Engineering, Conductive Polymers and Energy Applications Laboratory, Karaman*

[*]*bcarbas@kmu.edu.tr*

Abstract – It is clear that the new generation smart windows will develop much more in the coming years and in this sense, new multifunctional materials will be used in this field. While the easy use of such applications makes people happy, on the other hand, it also highlights energy efficient housing and transportation for humanity. There are some interesting parameters such as the control of daylight entering or leaving smart windows, self-power supply, and display functionality. Among the various chromogenic color changes, electrochromic methods are the fastest and easiest to control. Electrochromic materials are high-performance materials that are preferred both in the scientific world and in technological devices with their interesting electrochemical and optical properties. These materials can be inorganic or organic based, such as transition metal oxides, viologen systems and conductive polymers. Among them, electrochromic conductive polymers attract more attention with their superior mechanical, electrochemical and optical properties in portable electronics. Moreover, the ease and low cost of the synthesis procedures, as well as its low power and performance superiority, further solidify its rise among other materials in this sense. By modifying the chemical structures of conductive electrochromic polymers (or monomers) as desired, sharp and vivid color changes can be observed even at room temperature. The development of new electrochromic polymers can be with various modifications of the main chain, as well as side chain engineering, morphology control. Electrochromic properties of thin films of conductive polymers polymerized by chemical or electrochemical methods can be used in photo-electrochromic applications for information storage and various imaging purposes. In this study, it is desired to give information about conjugated polymers for self-powered electrochromic windows.

Keywords –Conjugated Polymer, Photo-electrochromic Device, Electrochromic Polymer, Smart Windows, Energy Efficiency in Buildings

I. INTRODUCTION

The word chromism is the fact that the material can change color reversibly due to any external effect. These external factors can be light (photochromic), steam (vapochromic), solvent (solvatochomic), heat (thermochromic), redox of material (electrochromic). For such materials, the color change is usually due to changes in the electron states of the molecules in the π or d orbitals of the electrons by various effects [1-2]. UV-vis spectrometers are the best characterization devices that can be used to observe the color change in the visible region. As a result of an electrochemical redox reaction, the material that can change the UV-vis absorption spectra shows electrochromic properties. Changes during the switching of the material as a result of oxidation and reduction reactions may extend to the near infrared region (NIR) as well as in the visible region [3-4]. These changes can even be observed in the thermal infrared and microwave regions. Therefore, observing a color change in a material may not be only in the visible region. Where in the electromagnetic region the color change can be detected by the detector during switching (that is, even if it is not in the region of the color change that the human eye can detect), there may be a color change in any case [5-6]. Electrochromic materials, namely chromophores, can be organic or inorganic based. Some transition metal oxides (molybdenum (VI) oxide, vanadium (V) oxide, niobium (V) oxide, iridium (III) oxide, tungsten (VI) oxide) and hexacyanometallates can be given as examples of inorganic based electrochromic materials. Tungsten oxide is the most widely used chromophore [7-9]. Organic-based chromophores (viologens and conjugated polymers) are less expensive and toxic than inorganic ones [10-13]. Organic-based chromophores also have the possibility of easy synthesis, such as making modifications of the properties (band gap, HOMO-LUMO energy value, morphology control) required for application on their chemical structures. Moreover, polymers have advantages such as obtaining flexible and light chromophores with their mechanical properties [14]. Some sources have divided electrochromic materials into three types according to their solubility in their redox states. Type 1 chromophores (some viologen-based materials) are soluble in both their oxidized and reduced states. Type 2 (on the other hand, is soluble in only one of the redox states and remains solid in the other state. Type 3 electrochromic materials (conjugated polymers) are in solid form in both redox states and are not soluble [3]. The most desired features for electrochromic materials used in technological devices are lightness, thickness, and ability to work at low power and easily transfer to the desired layer (printing, stamping, spray casting, dropcasting). In these respects, conjugated polymers constitute a good alternative to other inorganic based electrochromic materials. There is some energy consumption when coating electrochromic materials on the surface in various device applications. In electrochromic conjugated polymers, on the other hand, while the polymer changes color, there is less energy consumption compared to other electrochromes, since it requires some energy consumption only in the case of being charged [11].

A. *Important Paramaters for Electrochromic Polymers*

Conjugated polymers, as the name suggests, are organic macromolecules with a conjugated structure. Due to the delocalization of alternating single and double bonds in the main chain for any reason, the π-orbitals overlap, which causes the relevant polymer to have interesting optical and electrochemical properties. They can also have aromatic rings in their main chain backbone. Conjugated polymers have many applications besides their use in electrochromic devices. These are photovoltaic cells [15-16], sensors [17], energy storage devices [18], capacitors [19] and light emitting diodes [20] etc. In electrochromic applications, the properties of colors (hue, saturation, brightness intensity) must be specified exactly. There are many ways in order to synthesize conjugated polymers. Most popular ones are chemical and electrochemical synthesis. The synthesis type of conjugated polymer can affect optical and electrochemical properties of conjugated polymers. The chemical synthesis can be in two ways (organometallic coupling and treatment of an oxidative agent) for polymerization. Electrochemical oxidative polymerization method is studied with three electrode system (reference, counter and working electrode) in a monomer dissolved electrolyte solution with the help of potentiostat-galvanostat system. Polymer was coated on a working electrode via repetitive cyclic voltammetry or constant potential electrolysis methods. Deposition time, temperature, solvent/electrolyte/electrode type, scan rate, potential range during polymerization affect the morphology and optical properties of resulting polymer. Some important parameters (Band gap, HOMO/LUMO levels, π-π* transition wavelength, conductivity, charge carrier bands (polaron/bipolaron) were used in order to characterize a conjugated polymer. The conjugate polymer can be a homopolymer or a copolymer [21]. Sometimes, it may be necessary to make various optimizations in the energy levels of the polymer according to the application area in which the conjugated polymers will be used. In such a case, instead of altering the chemical structure of the initial monomer of the polymer, copolymerization may be an easier alternative way [22-24].

$$CE = \frac{\Delta OD}{Q_d} \text{.......................................(Equation 1)}$$

$$\Delta OD = log \frac{T_{oxidized}}{T_{bleached}} \text{..........................(Equation 2)}$$

It is important to reveal the electrochromic properties of a modified or designed conjugated polymer and compare them with its analogues. These parameters are maximum wavelength of the optical absorption (λ_{max}), optical band gap (E_g), switching time (t), the optical contrast (ΔT %), coloration efficiency (CE) and the appeared colors of the polymer in various doped states [11, 21, 25, 26]. In order to find the switching time, different potentials are applied to the studied electrochromic polymer and the maximum wavelengths in the absorption of the UV-vis behaviour are selected first, while it passes from the neutral state to the oxidized state. In the same way, two potentials where the polymer is the most colored and the bleached states are selected and the film is switched between at these potentials. On the other hand, the % transmittance (%T) graph against time for the relevant polymer at selected wavelengths is taken as data from the UV-vis spectrometer. With the graph obtained, the switching times of the polymer transitioning from the colouring state to the bleaching state or vice versa are calculated separately at the pre-selected wavelengths.

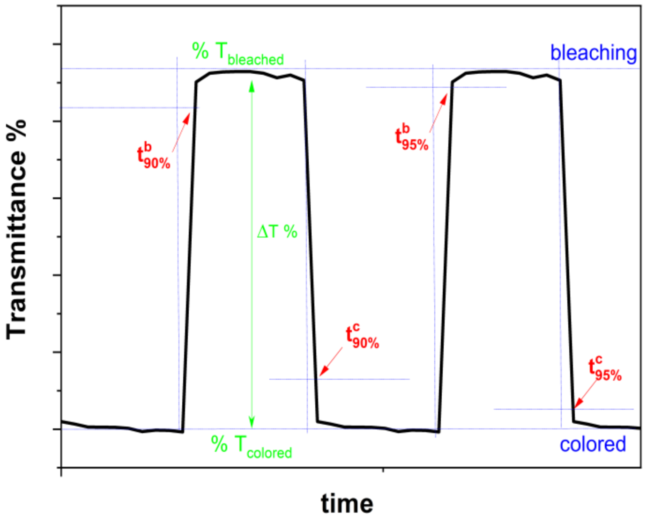

Fig.1 A switching graph (Transmittance % vs. time) at a selected wavelength for an electrochromic polymer.

Optical contrast (electrochromic contrast) value is also calculated with the same graphs above. The difference in transmittance values at between % $T_{bleached}$ (at fully oxidized state) and %$T_{colored}$ (at fully oxidized state) is called optical contrast (ΔT %). The coloration efficiency (CE) is found according to the formula in Equation 1 and 2 and is defined as the ratio between optical density change (ΔOD) to the unit charge density (Q_d) for polymer film during doping. Since the human eye can detect only 90% or 95% optical contrast, CE and switching time values for electrochromic polymer are calculated in these percent ratios (Figure 1).

B. *Color Engineering for Conjugated Polymers*

The great advantage of conjugated conductive polymers for applications in displays is that their colors can be modified just like an engineer by changing their chemical structure. Conjugated polymers, which can be equipped with a riot of colors, are open to synthesis procedures that enable reaching the target color with various design miracles. The color change depending on the polymer film thickness is the most difficult situation to explain in such polymers. The relationship between the polymer chemical structure and color should be established correctly and it should be aimed to reach the target color scale. Therefore, color control and color enginnering of polymer structures become very important in various device applications. Modification of the main or side chain structure for polymer can tune the color of conjugated polymer. Especially if color control can be achieved, sometimes with color mixing theory, a solution can be created with conductive polymers that can have a desperately hopeful color. In order to demonstrate this situation, the optical properties of the desired target polymer can be achieved by sometimes combining different groups (donor acceptor or donor acceptor-donor approaches or copolymerization) [11, 21, 23, 26, 27]. For this purpose, it is necessary to know the color theory, especially by using CMYK and RGB color mixing systems, the target color can be obtained. For example, a polymer that gives magenta and yellow colors in neutral state gives red color in neutral state when mixed in certain proportions. Color theory is a practical combination of art and science used to determine which colors look good together. The color wheel is the basis of color theory because it shows the relationship between colors. The color wheel, which shows the relationship between colors and helps in color harmony, forms the basis of color theory. There are two types of color wheels, RGB and CMYK (Figure 1). Additive color mixing theory is related with mixing of light. Red, blue and green, which are primary colors, can be coupled to form white magenta (red and blue), yellow (red and green) and cyan (green and blue). Subtractive color mixing theory is interested in dyes with three primary colors magenta, yellow and cyan. They can also combine in order to get colors in the visible light spectrum. By mixing the primary colors, the subtractive secondary colors black (magenta, yellow and cyan), red (magenta and yellow), blue (magenta and cyan) and green (cyan and yellow) can be obtained.

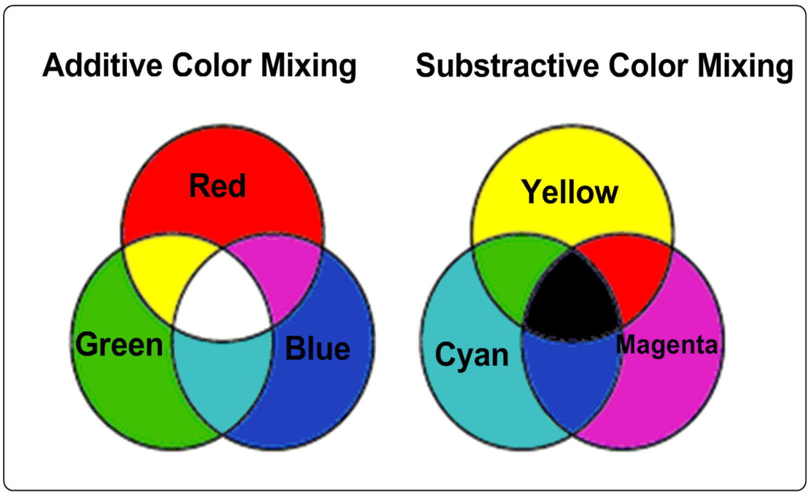

Fig.2 Representation of Color Mixing Theory. Additive Color Mixing (RGB); Substractive Color Mixing (CMYK)

A different application can be made by combining various mixtures to expand the color palette in the literature [27, 28]. Transition from color to colorless (transparent) is very important for electrochromic polymers used in display technologies [28-33]. Moreover, instead of synthesizing a single polymer in neutral state, by applying the subtractive color mixing theory, the desired color formation can be achieved with colors that complement each other [34-36]. Electrochromic polymers in the literature can be examined in three main groups [11]. They are named as anodically, cathodically colored polymers and multicolored electrochromic polymers.

Polymers that become colored in reduced state and colorless in oxidized state are called cathodically coloring polymers [37,38]. Poly(dioxythiophene)s (PEDOT and ProDOT) are usually in blue tones in the reduced state, while in the oxidized state they are transparent. In the opposite case of color transition, the polymer of interest is called as anodically colored polymer [39-41]. The polymers that give different colors at many applied potentials are multielectrochromic polymers [21, 25, 42-43] (Figure 3).

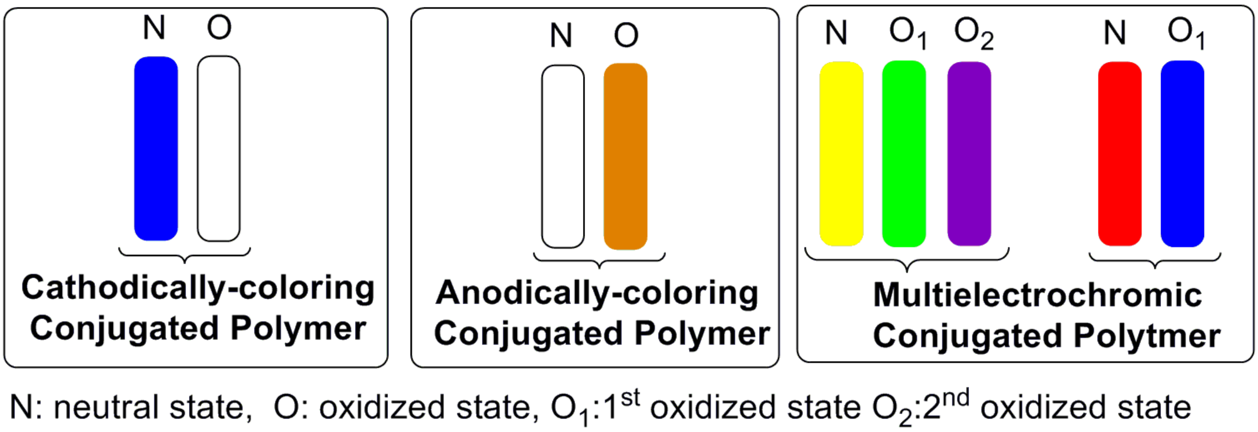

Fig.3 The classification of electrochromic conjugated polymers

(The colors shown are to represent the polymer color not given for a particular polymer. Polymers with white color were actually intended to be shown in transparent color.)

C. *Electrochromic Device*

Devices in which color can be changed with the effect of electric field created with electrochromic materials are called electrochromic devices. Such devices can be used in smart glasses, sensors, screens and in many areas for camouflage purposes. Electrochromic devices work in the same way as electrochromic materials. Conductive polymers are the most common materials used in such devices. A basic design for an electrochromic device is shown as in Figure 4. A basic electrochromic device consists of two electrode and a transparent gel electrolyte. Each electrochromic material is coated on an optically transparent electrode and their conductive surfaces faced each other. These two layers are sandwiched with a transparent gel electrolyte and the device is completed.

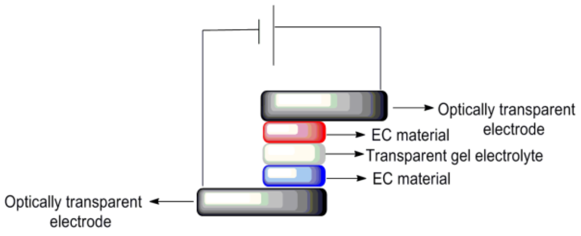

Fig.4 A basic design for an electrochromic device.

While inorganic materials have been extensively studied in electrochromic devices, conjugated polymers have also been synthesized and used in this kind of applications due to the advantage of high degree of color tailorability.

D. *Photo-electrochromic Device*

There are conjugated polymers used for self powered electrochromic windows. These windows and electrochromic devices requires electricity in order to change color. This energy can be supplied by renewable energy resource. While electrochromic reactions need energy for electrochromic devices, they cannot store energy. The phenomenon of electrochemically showing electrochromic properties when illuminated under daylight is called photo-electrochromism. Devices that operate according to this logic are called photo-electrochromic devices. The targeted state is actually a photovoltaic cell that converts daylight into electrical energy and a photo-electrochromic device that uses this energy to change the color of the electrochromic film. There are two types of photo-electrochromic device applications. First, for a non-sandwiched photoactivated system, a potential photoconductor required for electrochromism is provided (Devices acting in tandem with a photocell). Second, the electrochromic layer is sandwiched with a photoconductor (Photoconductive layers). In such devices, the electrical energy required to change the color of the electrochromic layer is compensated by the photovoltaic potential obtained by solar energy.

As the light hits the photoactive layer first and travels the minimum distance (front wall), it is taken from the back and travels a long distance (back wall), of course, will affect the performance of the device. It is desired that the light comes with the front wall (Figure 5).

Photoconductive materials are materials that are conductive only in light. Amorphous Silicon-based and some organic-based semiconductors are the most widely used. Electrons and holes, that is, charge carriers in the system, move from the valance band to the conduction band as a result of delocalization. These moving charges create the potential to cause color change for electrochromic materials.

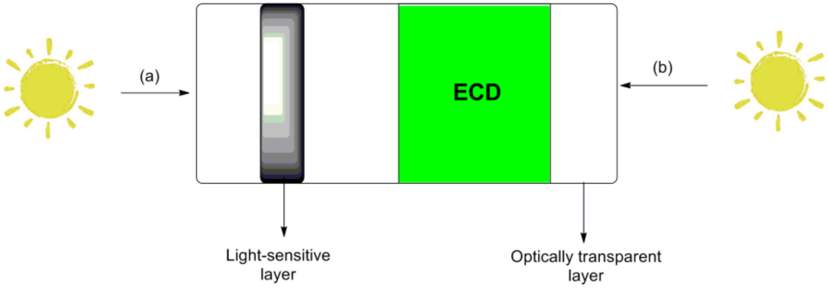

Fig.5 A schematic illustration of a photo-electrochromic cell. (a) front-wall illumination (b) backkwall illumination

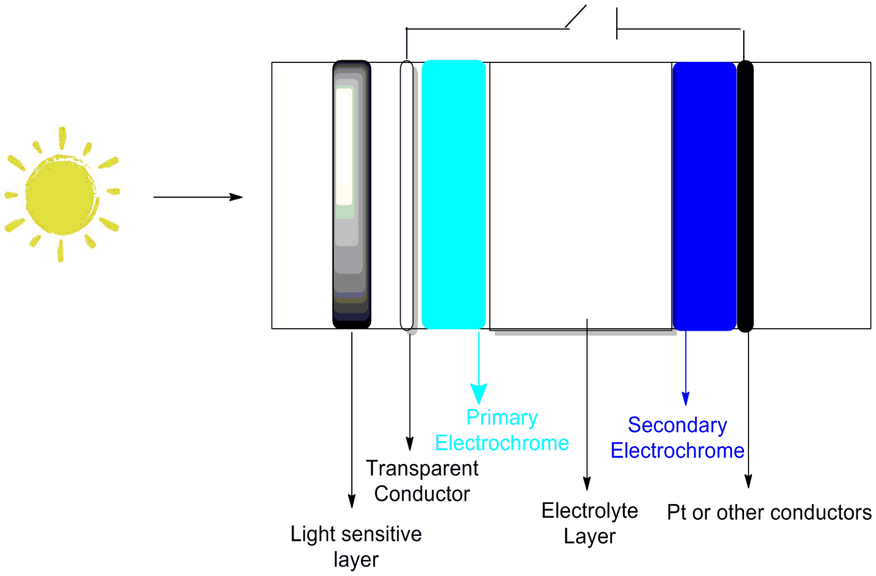

Fig.6 A schematic illustration of a photo-electrochromic cell. A photoconductive layer between the transparent conductor and the primary electrochrome layer.

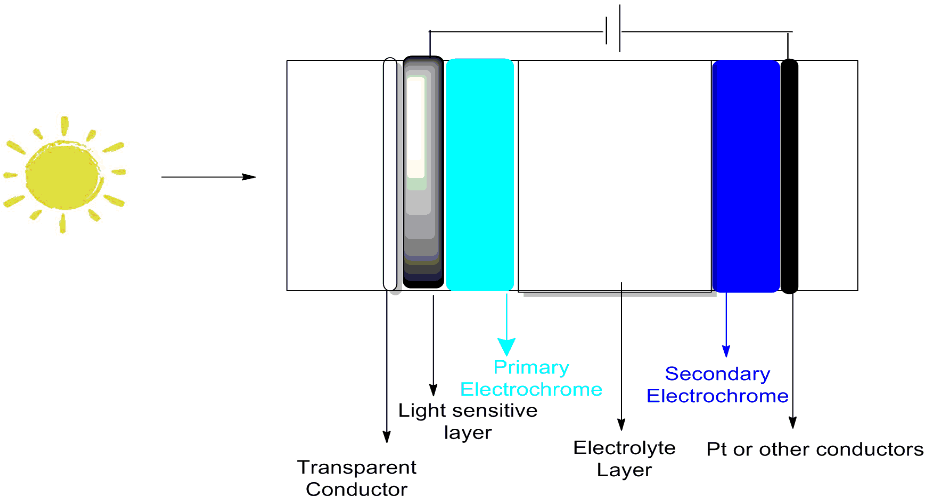

Fig.7 A schematic illustration of a photo-electrochromic cell. A photoconductive layer between the primary electrochrome layer and the electrolyte

Photoconductive material can be used in two ways in photoelectrochromic cells. First, the photoconductive part can be placed on the outside of the ECD and acts as a photocell switch. When the photoconductor sees light, it allows the electrochrome to change color and completes the circuit, and when it is dark, the coloring stops and the current stops (Figure 6). In the second system, this time the photoconductive layer accompanies the ECD and is placed between the transparent conductive layer and the electrochrome. During the electrochromic color change, electrolyte ions enter and leave the electrochromic layer, causing a color change. But electrons also enter the system with photoconductors. Since it is an opaque photoconductive layer, it has an effect on color change and both systems operate in reflective mode (Figure 7). Until now, very few such devices have been designed with conjugated polymers. The conjugated polymers, polyaniline (44-50), poly(pyrrole) (51), thiophene based polymers (52-53) were used in photoelectrochromic devices, as polymer electrochromes. For example, Ho and his co-workers were constructed a dual electrochromic device/ dye synthesized solar cell (photo-electrochromic cell) in one device and showed higher coloration efficiency value than that of WO_3 based photo-electrochromic device [53]. They also were constructed a device, which consists of poly (ProDOT-Et_2) as an electro chrome in their device and obtained achieved reasonable optical contrast value (~34%) [54].

II. CONCLUSION

Solar energy, which is a renewable energy source, is the cleanest and cheapest energy source. Many scientists work hard to transform this energy into different alternative energy sources. Especially in summer, there is a lot of energy consumption for the cooling of houses that are heated by solar energy. Not to mention the money spent on glass protectors and textile products used to take this precaution. The amount of energy consumed for heating, cooling, lighting and ventilation of buildings constitutes a large slice of the energy consumed globally. From this point of view, it becomes very meaningful to be able to prevent the energy consumption of the houses. One of the ways to reduce the energy use required for lighting and cooling of houses is the use of smart window technology in houses. In this study, photoelectrochromic devices that take their own energy from the sun and thus change the color of the glass by electrochemical ways are discussed in order to become energy efficient. These self-powered switchable devices is constructed with electrochromic materials (metal oxides, viologens or conjugated polymers) Among them, conjugated polymers attracts the attention of the scientific world. Because the chemical structure modification of such materials is possible when compared to inorganic bases and devices designed with such materials provide high optical contrast, coloration efficiency and low switching time

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