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Electrochemical study of dual conjugated polymer electrochromic devices

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Abstract

A new methodology for the electrochemical characterization of any device constituted by two electroactive films of conducting polymers, such as electrochromic windows, artificial muscles, polymeric batteries or supercapacitors, is proposed. During electrochemical characterization of dual polymer devices, the charge consumed by the device and the independent potential evolution vs. a reference electrode (oxidation states) of the two constituent materials are followed. The charges consumed inside and outside the electrochromic potential window of each polymer are measured, therefore obtaining percentages of efficient and inefficient charge. Dual polymer electrochromic systems were constructed and characterized by potential sweeps. The influence of the applied potential limits, the redox charge ratio between the two constituting films, or the starting oxidation state of each material on the final percentage of efficient charge consumed by each electrode were studied.

Keywords: Electrochemical characterization; Electrochromic devices; Conjugated polymers; PEDOT; ProDOT

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1. Introduction

The ability of conducting polymers to electrochemically modify their physical or chemical properties such as volume, color, stored charge or porosity has been used to develop different electrochemical devices, like artificial muscles [1–5], electrochromic displays [6–11], smart membranes [12–16], polymeric batteries [17] and supercapacitors [18]. Although device architectures will vary upon the desired functionality, they are all electrochemical cells. An external flow of electrons promotes oxidation (or reduction) at one electrode, with simultaneous transport of charge across the electrolyte and polymer/electrolyte interfaces. Reduction (oxidation) of the opposite electrode completes the cell reaction. From this perspective, the use of a configuration consisting of two complementary electroactive polymeric electrodes appears as an efficient way of improving the characteristics of the devices, since both electrodes modify their properties simultaneously contributing to an enhanced performance. This configuration has been proven to be efficient for artificial muscles [2,19–21] or dual-type electrochromic displays [8,9].

On the other hand, the functionality of a device is expected to be directly linked to the redox processes taking place inside its constituent electrodes. For every conducting polymer/electrolyte system these processes take place along a defined potential range. The polarization of the polymer at potentials beyond this range will be inefficient in terms of change of the desired properties. Furthermore, this can promote additional processes of overoxidation or degradation of the polymer. This subject has been widely studied [22–25], and the degradation mechanisms proposed include nucleophilic attacks, crosslinking [26] or chemical attack from the electrolytic medium [27].

During the operation of a device, information about the instantaneous oxidation state (potential vs. a reference

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electrode) of each polymeric electrode will help to know the material state and the risks of overoxidation of the active material, as well as to optimize device performance. Electrochemical techniques able to provide this information, such as cyclic voltammetry or chronoamperometry, are usually employed in a three electrode cell configuration, applying a known potential to one of the electrodes (working electrode, WE) referred to a second one (reference electrode, RE). The remaining electrode (counter electrode, CE) allows current to flow and complete the cell reaction, attaining the necessary potential. These techniques are useful for obtaining information about the redox potential window of the material, or the consumed redox charge. When applied to dual type configurations, these techniques present a main problem: information about the oxidation state is restricted to the working electrode, and the potential achieved by the counter electrode is not controlled.

A different approach uses a two electrode cell, in which a potential difference is applied between both electrodes. This configuration is closer to real-life operation conditions, but in this case none of the oxidation states of each constituent material is known during operation of the device.

Here, a two-step methodology for studying dual conjugated polymer systems is proposed, consisting of an independent voltammetric characterization of the two constituent materials before assembling them to construct a dual system, followed by the measure of their electrochemical parameters (oxidation state, charge consumed) during operation as part of a dual system device. This is possible due to the inclusion of a reference electrode while the system is working in a two electrode cell configuration. An analysis of the electrochemical parameters, obtaining the percentage of efficient and inefficient charge consumed by the two electrodic materials, provides relevant information in order to optimize the device performance and to maximize the lifetime of the electroactive materials.

The proposed methodology is described, and applied to different practical cases. Electrodes, materials and configuration of the systems were chosen to be used as electrochromic devices, though the methodology is not limited to these systems.

2. Experimental

2.1. Materials

Lithium trifluoromethanesulfonate ($LiCF_3SO_3$) from Aldrich was used as received. Acetonitrile (ACROS) was purchased from Fisher scientific and distilled over calcium hydride. An Ag/Ag^+ non-aqueous reference electrode (10 mM $AgNO_3$, 0.1 M tetrabutylammonium perchlorate (TBAP) in ACN; 0.456 V vs. normal hydrogen electrode) was used. All the films were prepared on indium tin oxide (ITO) coated glass plates of nominal resistance $R =$ 15–25 ohms and surface area $S =$ 3.5 cm^2, purchased from Delta technologies. 3, 4-Ethylenedioxy-thiophene (EDOT) was purchased from Aldrich and distilled under reduced pressure before use. 3,6-Bis(2-(3,4-ethylenedioxy)thienyl)-*N*-methylcarbazole (BEDOT-NMCz) was synthesized as reported earlier [28]. 3-(Biphenyl-4-ylmethoxymethyl)-3,4-dihydro-2H-thieno(3,4-*b*)-(1,4)dioxepine (BPMOM-ProDOT) was kindly supplied by Prof. Kumar and details of its synthesis can be found elsewhere [29]. The structures of monomers used are represented in Fig. 1.

2.2. Equipment

A CHI 660 potentiostat was used as the potential source to apply the specific potentials to the device, while a 9000 Keithley Digital Multimeter recorded the potential of one of the conjugated polymers against the reference electrode at any given time. The data from the multimeter were collected using Labview software. The electrochromic characterization of the polymers was made using a UV–vis Dinko Instruments 8500 spectrophotometer.

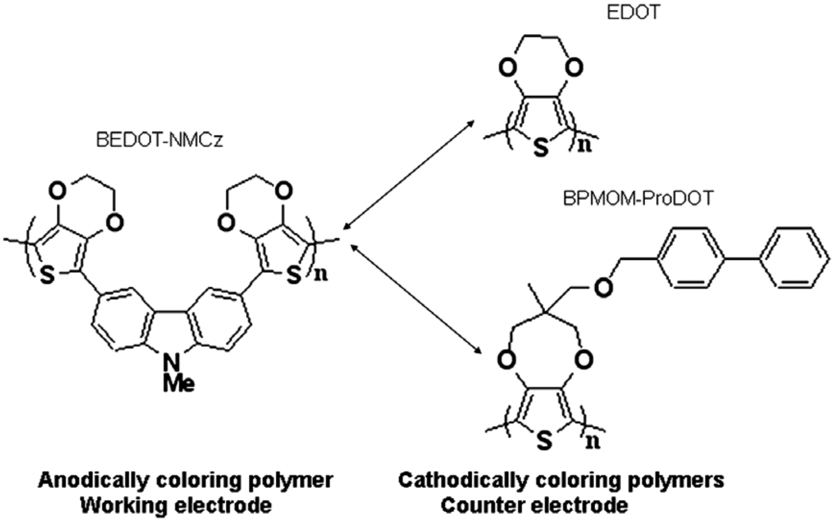

Fig. 1. Structures and notation of the polymers used. Arrows represent combinations used for dual polymer type configuration devices.