Materials Science & Engineering B 228 (2018) 167–174

Contents lists available at ScienceDirect

Materials Science & Engineering B

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

Review

Materials and processing of polymer-based electrochromic devices

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ARTICLE INFO

Keywords:
Organic electronics
Electrochromic devices
Conjugated polymer processing

ABSTRACT

The demand for polymer based electrochromic device is increasing in recent years due to not only the advantages of conjugated electrochromic polymers such as high color versatility, large optical contrasts, but also their potential applications in flexible devices. In this review, we focus on the state-of-the-art research activities related to the materials and assembly techniques developed for polymer based electrochromic devices. More specifically, we will give an overview of the whole fabrication process including transparent conductive substrate, processing of electrochromic polymer, electrolyte formulation, as well as edge sealant materials and possible encapsulation methods.

1. Introduction

Within the development of organic electronic devices, electrochromic devices (ECDs) provide new opportunities for industrial applications [1]. Electrochromic materials change their color due to electrochemical reactions. Under the influence of externally applied voltages, the optical characteristics of the material are changed reversibly, and in some cases, multiple color states are observed upon different electrochemical potential [2]. Electrochromic materials can be divided as inorganic metal oxide materials or organic materials. They can also be classified in three different categories depending on their physical state at room temperature, namely: Type I are soluble and remain in the solution during usage; Type II are soluble in their neutral state and form a solid on the electrode after electron transfer; and Type III are solid and remain solid during usage [3,4].

Three groups of electrochromic materials are most commonly used in making electrochromic devices: metal oxide films [5] (inorganic Type III), conjugated polymers (organic Type III) and molecular dyes [6] (mainly viologen based organic Type I). Conjugated polymers began to stand out among others (including metal oxides and viologens) due to the ease of manipulation of properties through structural modifications, facile preparation, flexibility and low cost [7]. In terms of their electrochromic (EC) performance, conjugated polymers (ECPs) present high color versatility, large optical contrasts, rapid response times, and require low power consumption during operation. Through synthetic modifications of the 3,4-alkylenedioxythiophene family of polymers, Reynolds' group has recently completed a full color palette that spans from yellow, orange, red, magenta, blue, cyan, green, and black. The color tuning was realized by utilizing electron rich and donor–acceptor repeat units, electron-donating substituents, and steric interactions [8]. The demand for conjugated polymer based electrochromic device owes to the increasing interest in industrial applications. These applications include smart windows, optical shutters in airplanes, rear view mirrors in automobile, sunglasses as well as reflective displays [9]. Many studies focused on smart window structure as an application of polymer electrochromic technology, which applies the basic 7-layer EC device architecture (Fig. 1) [10,11] (Ref. [10] treated glass/ITO as a single layer, but we treat them here as two layers because different substrate and transparent electrode materials can be used). In the past, various fabrication methods related to smart windows have been studied, such as chemical vapor deposition (CVD) and sputtering processes. Additionally, various limitations caused by the necessary high temperature and vacuum still exist in fabricating ECDs [12] (Fig. 2).

Recently, Xu's group published a review focusing on the synthesis methods for polymer electrochromic materials through the design of building blocks [13]. Krebs's group summarized the electrochemical and optical properties of organic electrochromic materials [14]. Although these review articles provide comprehensive information on the ec materials preference, more information is needed on the fabrication and packaging of ec devices. In this review paper, the various methods and related materials to fabricate conjugated polymer based EC devices are listed and discussed. More specifically, we will give an overview of the whole fabrication process including transparent conductive substrate, processing of EC polymer, electrolyte, device assembly using sealant materials and possible encapsulation methods.

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https://doi.org/10.1016/j.mseb.2017.11.016
Received 10 July 2017; Received in revised form 11 November 2017; Accepted 15 November 2017
0921-5107/

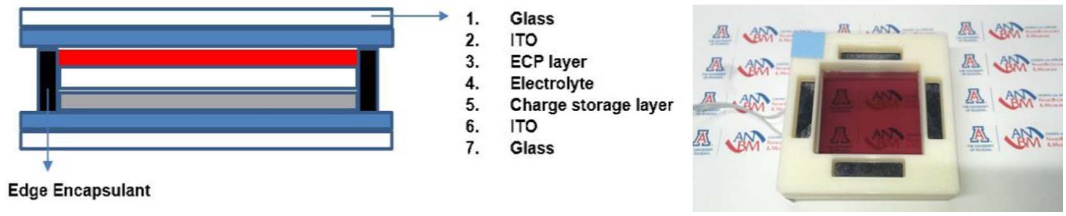

Fig. 1. Left: Typical polymer EC device architecture for glass/ITO substrate. From top to bottom, the 7 layers are glass/ITO/ECP/electrolyte/charge storage/ITO/glass where ito serves as the transparent electrode and glass is the substrate material; Right: a magenta color EC device consist of the 7-layer structure, which was fabricated at the Center for Applied Nanobioscience and Medicine. The magenta EC polymer was provided by Dr. J.R. Reynolds' group at Georgia tech, and the device was assembled according to Ref. [10].

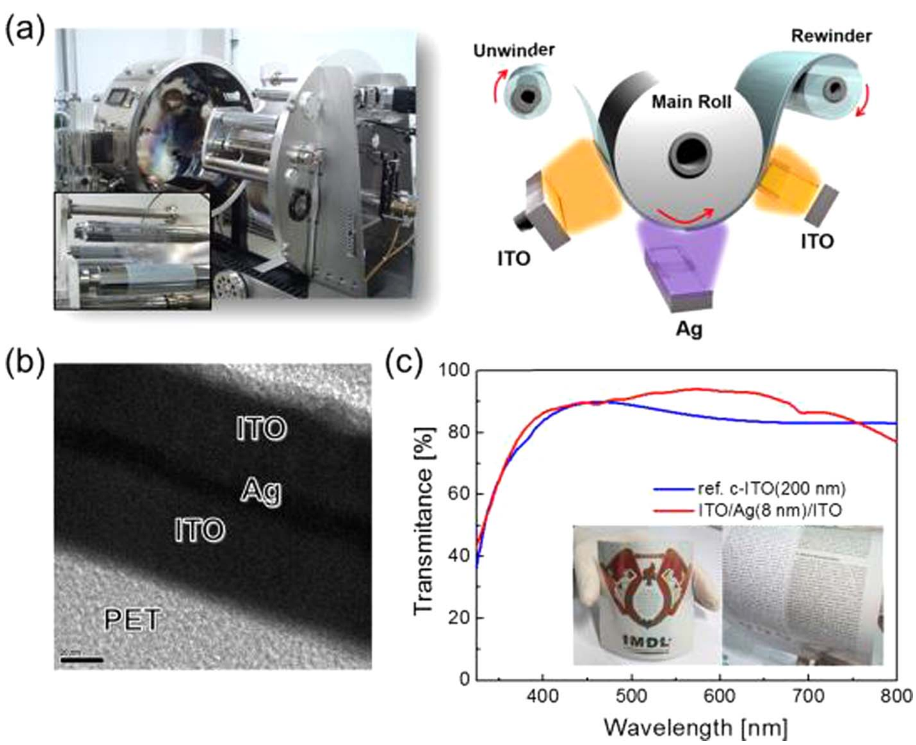

Fig. 2. Roll-to-roll (R2R) sputtering system and the characteristics of transparent ITO/Ag/ITO electrode coated on flexible Polyethylene terephthalate (PET) substrate. (A) Photograph and schematic of the lab-scale R2R sputtering system. The inset shows an uncoated pet film on the winding roller. (B) Cross-sectional tem image of the R2R-sputtered multilayer. (c) Optical transmittance of 200 nm ITO reference film and an multilayer electrode. Reproduced from Ref. [19] with permission from Elsevier B.V.

2. Transparent electrode

The most commonly used electrode material in electrochromic devices is indium-tin-oxide (ITO) [15] deposited on glass substrate. In the early stage of the development, the deposition of ITO was mainly by vacuum evaporation of In/Sn metal or by sputtering techniques such as DC diode and Radio Frequency sputtering of metal alloy targets. Post oxidation was necessary and the process required a high temperature reaching 400–500 °C. Later on, deposition starting with a partially oxidized or fully oxidized material instead of metal or metal alloy was found to be a more controllable process. Nevertheless, due to the sacristy of Indium, alternative transparent conducting oxides (TCOs) materials have been developed such as Fluorine doped Tin Oxide (FTO) [16] and Aluminum doped Zinc Oxide (AZO) [17]. A disadvantage of these TCOs is that their electrical conductivities are relatively low comparing with ITO [18]. Recent, a promising direction for high performance transparent electrode is the multilayer transparent electrode that showed high electrical conductance and optical transparency, fabricated by a roll-to-roll (R2R) sputtering method [19].

Despite recently development, limitations still exist for TCOs, such that the deposition techniques are expensive, and TCO films are brittle, which is not ideal for flexible electronic applications. While suitable for windows and mirrors, features such as being flexible [5,20] and bendable [21] are required for applications such as paper-like displays and wearable device [22–25]. For these reasons, flexible electrodes alternative to TCOs such as organic polymers and nanomaterials have been investigated [26–29]. Many attempts have been focused on using carbon-based nanomaterials such as graphene [30,31] and carbon nanotubes (CNTs) [32,33]. The features of these materials, such as transparency, electrical conductivity, and chemical stability make them an promising electrode alternative for ECDs [34]. Recent studies have claimed good electrochromic features such as fast color-switching speed, good cyclic stability, and high coloration efficiency. In recent examples, flexible ECDs were fabricated using graphene-coated PET [35]. In another study, multilayer graphene was employed not only as the electrode, but also integrated as the active EC layer [24]. Polymer-based ECD have also been assembled using single-walled carbon nanotubes on glass as electrode substrates [36]. Another promising substitute is organic conductive polymers such as Poly(3,4-ethylenedioxythiophene) (PEDOT) or and its derivatives [37]. Among the organic polymers, poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) is the leader in transparent conducting polymers with high electronic conductivity [38].

Besides carbon based alternatives and organic conducting polymer alternatives, metal nanowire is a new focus for ECDs assembly. Krebs et al. reported an ITO-free ECD using flexoprinted silver grids as the electrode [39]. Later on, further improvements were made by embedding the silver grid into the substrate [27], and the ECDs showed improved optical contrasts and switching times. Recently, Lexan [38] and Kapton [38] substrates have been developed for flexible electrochromic