

Comparison of performance parameters of poly(3,4 ethylenedioxythiophene) (PEDOT) based electrochromic device on glass with and without counter electrode

S SINDHU*, K NARASIMHA RAO[†] and E S R GOPAL^{††}

Practice School Division, BITS Pilani; Professional Development Centre, Bangalore 560 008, India

[†]Department of Instrumentation, ^{††}Department of Physics, Indian Institute of Science, Bangalore 560 012, India

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Abstract. Conjugated polymers are promising materials for electrochromic device technology. Aqueous dispersions of poly(3,4-ethylenedioxythiophene)-(PEDOT) were spin coated onto transparent conducting oxide (TCO) coated glass substrates. A seven-layer electrochromic device was fabricated with the following configuration: glass/transparent conducting oxide (TCO)/PEDOT (main electrochromic layer)/gel electrolyte/prussian blue (counter electrode)/TCO/glass. The device fabricated with counter electrode (Prussian blue) showed a contrast of 18% and without counter electrode showed visible contrast of 5% at 632 nm at a voltage of 1.9 V. The comparison of the device is done in terms of the colouration efficiency of the devices with and without counter electrode.

Keywords. Electrochromic devices; conducting polymers; PEDOT; indium tin oxide.

1. Introduction

Electrochromic windows consist of up to seven layers of materials. The function of the device results from the transport of hydrogen or lithium ions from an ion storage layer and through an ion conducting layer, injecting them into an electrochromic layer. The presence of the ions in the electrochromic layer changes its optical properties, causing it to absorb visible light resulting in darkening of the window with a very low applied voltage (Skotheim *et al* 1995). Most commonly used electrochromic materials are tungsten trioxide (WO₃) and iridium dioxide (IrO₂) (Mortimer 1997).

Here we make use of the property of electrochromism of conducting polymers which makes them important for use in smart windows, as discussed by Granqvist (Svensson and Granqvist 1984). These smart windows have important applications like the regulation of incident solar energy and glare for the improvement of energy efficiency of buildings, vehicles, aircraft, spacecraft and ships (Granqvist 1988; Lampert 1992) as well as electrochromic eye glasses. Conducting polymers are receiving attention because of their use in sensors, actuators, LEDs, electrochromic devices, etc (Skotheim *et al* 1998; Mortimer 1999). Polythiophene is unique due to its environmental stability (Kareiyama and Nalwa 1997; Kros *et al* 2001). Electrochromic devices utilizing conjugated polymers as

electrochromic layers have gained increasing attention owing to their optical properties, fast switching times and contrast ratios, allowing a number of applications such as antistatic coatings, electrode materials, sensors, electrochromic windows and electronic paper (Roncali 1992; Welsh *et al* 1999; Groenendaal *et al* 2000a; Argun and Reynolds 2005).

We use polyethylene dioxythiophene [PEDOT] as our electrochromic polymer. These polymers can adhere to the electrode surfaces, are highly conducting, while the undoped neutral forms are insulating. The oxidized (doped) and reduced (undoped) states of these polymers exhibit different colours, and electroactive conducting polymers are all potentially electrochromic as thin films. PEDOT changes its colour from opaque blue in its reduced state to transparent light green in the oxidized state (Groenendaal *et al* 2000b). This colour change is desirable in fabrication of smart windows and display devices (Monk *et al* 1995; Rosseinsky and Mortimer 2001).

In this paper, we have fabricated a small area electrochromic device using PEDOT as the electrochromic layer onto TCO coated glass substrate with different configurations. The usage of TCO coated glass substrates as electrode enhances the properties for its use in patterned displays.

The electrochromic device consists of six to seven layers, with transparent conducting oxides coated with electrochromic material sandwiched between a liquid, solid or gel electrolyte. The counter electrode is chosen so that it has to be either colourless in both oxidized state and reduced states or electrochromic in a complementary

*Author for correspondence (sindhunair@bits-pilani.ac.in)

mode to the main electrochromic layer. The counter electrode also increases the efficiency and contrast of the device which is discussed here. The electrochromic layer here is poly 3,4-ethylenedioxythiophene which is synthesized and characterized (Kumar *et al* 1998; Krishnamoorthy *et al* 2002) by our partner group in the Indian Institute of Technology, Mumbai. The counter electrode chosen here is Prussian blue. The electrochromic studies of conducting polymers have been carried out since 1983 (Yoshino and Inuishi 1983; Kobayashi *et al* 1984; Mastrogostino *et al* 1989; De Paoli *et al* 1990; Rodrigues *et al* 1991) mostly with liquid electrolyte. A recent survey done by Granqvist *et al* (2003) gives a clear picture about the present electrochromic device research and activities. Here we have attempted the fabrication of electrochromic device (ECD) with a new combination using gel polymer electrolyte and with and without counterelectrode. The electrochromic switching phenomena of these devices have been studied.

2. Experimental

Transparent conducting oxide was deposited in a 19" diameter Edwards's high vacuum unit. Thin films of indium tin oxide (ITO) were coated using 90% indium and 10% tin by wt. as the starting materials. High vacuum was created in a deposition chamber using a diffusion pump backed by a rotary pump, and the base pressure obtained was 1×10^{-5} mbar. The pressure maintained during the deposition was 1.5×10^{-4} mbar. Oxygen was passed through the hollow type (Ebert-type) (Ebert 1983) discharge source, and was ionized. A discharge current of 160–165 mA was maintained during deposition of the films. Source materials were taken in a graphite insert, melted homogeneously and evaporated using an electron beam

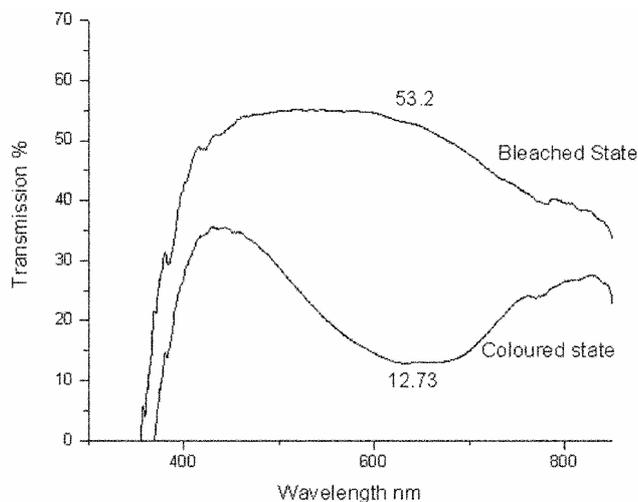


Figure 1. Transmission spectra of spin coated PEDOT film showing ~40% transmission at 632 nm, 1.9 V.

gun on to clear glass substrates, pre-cleaned using laboratory detergent, washed with running water, and rinsed in distilled water. The substrates were dried and subjected to ionic bombardment for 10 min in a vacuum prior to deposition. Film thickness and rate of deposition were controlled using a quartz-crystal thickness monitor. The rate of deposition maintained during the deposition of the films was 1.5–2 Å/s. Indium tin oxide thin films of sheet resistance, 25–30 ohm/□ and ~90% transmission on glass substrate, were achieved and used here.

Thin films of the electrochromic layer, PEDOT [1% ethylene dioxythiophene (EDOT), 1% poly (styrenesulfonate) (PSS), 2.5% polyvinyl acetate (PVA) with viscosity 2000 centi Poise] was coated onto the transparent conducting oxide layers by means of a spin coating technique. The polymer was spin coated onto TCO coated PET substrates at a rate of 1000 rpm in 10 s and further annealed at around 80°C. The adhesion of the polymer onto the substrates depends critically on the physical properties of the transparent conducting oxides. Uniform polymer films of 10 μm thick were obtained and used for further studies. The thickness of the polymer film was found using a profilometer by making a step in the film.

The counter electrode chosen, Prussian blue, was coated onto TCO coated substrates by the method of electro-

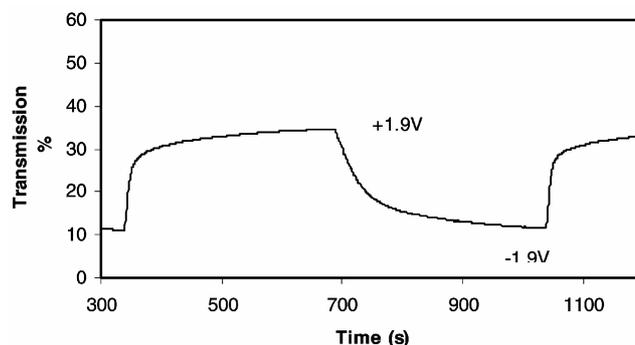


Figure 2. Transmission spectra of the device (glass substrate) with counter electrode in the coloured and bleached states showing ~21% contrast at 632 nm, ± 1.9 V.

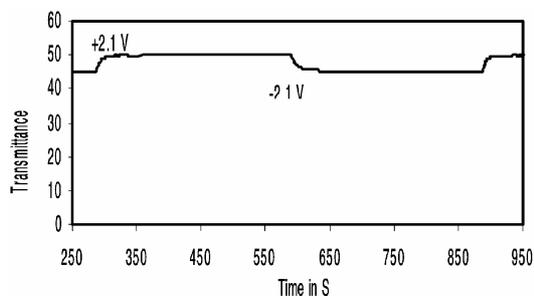


Figure 3. Transmission spectra of the device (glass substrate) without counter electrode in the coloured and bleached states showing ~21% contrast at 632 nm, ± 1.9 V.

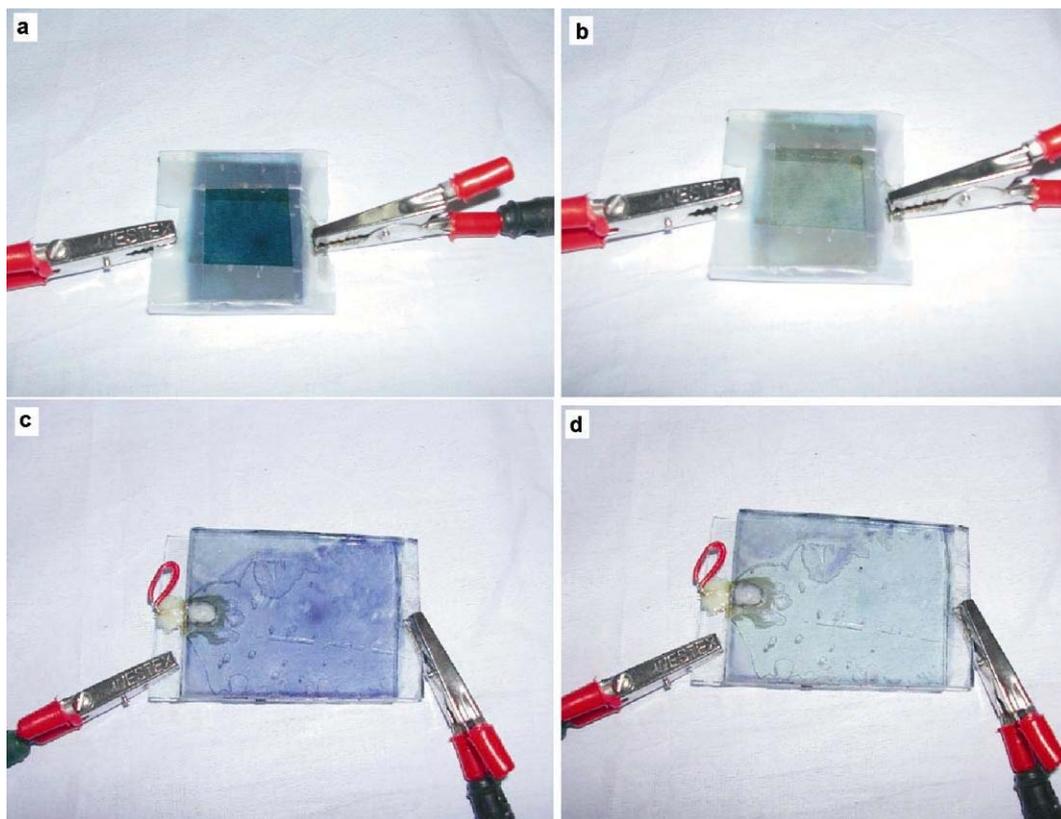


Figure 4. The fabricated device with PEDOT in the coloured and bleached states **a.** with counter electrode coloured state, **b.** with counter electrode bleached state, **c.** without counter/electrode coloured state and **d.** without counter electrode bleached state.

deposition. Prussian blue film on the TCO substrates was electrochemically deposited under the galvanostatic conditions of an equivolume mixture of 10 mmol/L FeCl_3 and 10 mmol/L $\text{K}_3[\text{Fe}(\text{CN})_6]$ aqueous solution. A 1 M polymer gel electrolyte was synthesized by using lithium perchlorate in propylene carbonate and polymethyl methacrylate (PMMA). 1 M Lithium perchlorate with the polymer, PMMA (15 wt.% with respect to the weight of the liquid electrolyte) was dissolved in propylene carbonate of a given strength by continuous stirring, accompanied by simultaneous heating at 80°C to obtain a transparent and homogeneous gel electrolyte.

A seven-layer electrochromic device is designed (ITO/PEDOT/Gel/Prussian blue/TCO) and fabricated.

The transmission spectra of the spin coated PEDOT film onto TCO coated glass in liquid electrolyte (lithium perchlorate in propylene carbonate) is given in figure 1 recorded using an OCEAN OPTICS spectrophotometer. This film showed a contrast of $\sim 41\%$ at 632 nm and with a voltage of 1.9 V.

The fabricated devices were characterized using a computer controlled setup consisting of a He-Ne laser source ($\lambda = 632.8$ nm), a Si photo detector together with a versatile micro-controller based ECD characterization unit. Multiple step potential cycling was performed by

applying a square wave potential of amplitude, 1.5 V, at a fixed frequency of 0.0011 Hz. Figure 2 shows the transmission spectra of the device with counter electrode in the coloured and bleached state. The voltage applied is 1.9 V. Transmission of the device in the bleached state, T_b and in coloured state, T_c , measured at 632 nm is T_b , 35.14 and T_c , 11.02, resulting in a contrast of $\sim 21\%$. The PEDOT film as a device gave low contrast compared to the film. The area of the device was ~ 15 cm². Using these values the colouration efficiency of the device was calculated which is defined as the change in optical density divided by the charge density of the colouration process. Colouration efficiency is calculated by the equation

$$\text{CE} = \log(T_b/T_c)/(Q/A),$$

where Q is the charge intercalated/deintercalated and A the area of the film. Colouration efficiency of the device by colouring it with a slow period of 70s with cathodic charge intercalated, 0.355 mC/cm², was calculated to be 212.5 cm² C⁻¹.

Figure 3 shows the transmission of the device without counter electrode. The optical response at the maximum absorption wavelength of 632.8 nm by the application of square wave potential showed a contrast of $\sim 5\%$. This gave a colouration efficiency of 4.2 cm²/C with a charge

Q of 0.14C and area of the device was 11.9 cm². The device switching time from coloured state to bleached state is found to be ~20 s. The devices were tested by giving a high delay time of 500 s to check its stability in the coloured and bleached states. The response time of the electrochromic device is smaller than that of the film tested in an electrochemical cell, as the cathodic process at the transparent conducting oxide is slower than the PEDOT doping. It was observed that the device when kept in the coloured state for a long time influenced the bleaching time. High colouration efficiency gives large optical modulation with charge injection or extraction and is an important parameter for electrochromic devices. Here we have showed clearly the influence of a counter electrode in the device performance. Figure 4 shows the device with and without counter electrode in the coloured and bleached states.

3. Conclusions

Uniform films of PEDOT were deposited onto the transparent conducting oxide coated glass substrates. It was observed that the adhesion and uniformity of the film depend critically on the sheet resistance and cleanliness of the substrate material. The device with counter electrode showed a comparatively higher contrast than the device without counter electrode. The device also showed the ability to operate at a very low voltage of 1.9 V. Both the devices showed almost same order of switching time. This focuses on the possibility of fabricating large area electrochromic device with polymers and with counter electrode to get a fast switching time, high contrast and good colouration efficiency by possibly reducing the thickness of the film, controlling the resistance of the electrodes and electrolyte so as to reduce the intercalated and de-intercalated charges.

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