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Low cost quasi solid state electrochromic devices based on F-doped tin oxide and TiO_2

H.N.M. Sarangika [a,*], M.A.K.L. Dissanayake [b,c], G.K.R. Senadeera [b,d], W.G.M.D. Karunarathne [a]

[a] Department of Physical Sciences and Technology, Sabaragamuwa University of Sri Lanka, Sri Lanka
[b] National Institute of Fundamental Studies, Hantana Road Kandy, Sri Lanka
[c] Postgraduate Institute of Science, University of Peradeniya, Sri Lanka
[d] Department of Physics, The Open University of Sri Lanka, Nawala, Nugegoda, Sri Lanka

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ABSTRACT

In recent past, electrochromic devices (ECDs) have attracted much attention due to their potential applications as display devices with low power consumption. In the present study, we investigated the possibility of replacing expensive WO_3 and CeO_2 with low cost, transparent and nano-crystalline, titanium dioxide (TiO_2) as the electrochromic material and F-doped tin oxide (FTO) glass substrate as the counter electrode respectively. A quasi solid polymeric electrolyte composed of lithium chloride (LiCl), was employed as the electrolyte. The device changes its transmission between 63% (bleached state) and 0.98% (colored state) at the wavelength of 600 nm at 3.7 V.

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1. Introduction

Over the last few decades electrochromic devices (ECDs) have attracted much attention due to their usage in modern applications such as electrochromic windows, shades, visors and rear view mirrors in auto mobiles, display pannels, etc [1,2]. An EC device mainly consists of three major components; an active electrode of electrochromic material, an electrolyte and a counter electrode. Even though there are a number of materials that exhibit electrochromic property, not all of them are of commercial importance. Out of these materials tungsten oxide (WO_3) has been the most extensively studied material used in ECDs. However, the electrochromic performance and the reversible coloration under double injection of ions and electrons of tungsten oxide depend strongly on its preparation methods and the structure. In general, WO_3 thin films with high coloration efficiency are mostly obtained by either using vacuum evaporation [3–5] or sputtering techniques [6]. However, these methods are expensive, time consuming and difficult to adopt for the deposition onto large-area substrates. Among other materials which exhibit the electrochromic properties, TiO_2 could be a possible candidate for replacing the expensive WO_3 due to

its salient features such as low cost, natural abundance and minimum environmental problems. Further, transparent thin films of TiO_2 can be fabricated using simple techniques such as doctor blading, screen printing, spraying etc. By taking into account all the aforementioned factors we have focused our attention on the fabrication of a novel type of electrochemical device using TiO_2 as the electrochromic material.

In ECs, V_2O_5, CeO_2 or their derivatives are the most commonly used materials for the counter electrode. Particularly, CeO_2 alone exhibits good transparency in reduced and oxidized states in the visible region and shows strong absorption of light below 380 nm with good reversibility for lithium intercalation. However, its charge capacity is too low for a counter-electrode in electrochromic devices [7]. Although the charge capacity of the V_2O_5 is appropriate to be used as a counter-electrode, during lithium intercalation an unfavorable brownish-grey coloration occurs [8]. Again, apart from these facts, the availability, cost and the complications in preparing these thin films should be taken in to account for large scale production of ECDs using these materials. Due to these reasons, tin oxide (SnO_2) which has been an intensively studied semiconducting material for numerous applications and posses unique properties such as high optical transmittance together with high conductivity could be a good candidate to be used as the counter electrode in ECDs. In this study we have explore the

* Corresponding author.
  E-mail address: sarangikah@appsc.sab.ac.lk (H.N.M. Sarangika).

possibility of using F-doped tin oxide (FTO) glass substrate as the counter electrode.

Apart from these electrodes, the other main component, the electrolyte, employed in ECDs is also crucial for the improved efficiency and long term stability of these devices, especially due their role in ion transport inside the device. Since most of the efficient ECDs consist of liquid type electrolytes, their practical applications are limited due to several technological problems, such as durability, leakage, relatively poor long term stability generally associated with some chemical constituents of these electrolytes and the presence of water and volatile solvents. Therefore, alternative electrolyte materials have to be developed in order to overcome these problems and to improve the long term operational stability of the EC devices. Especially, the volatile nature of solvents present in the electrolyte causes significant technological problems associated with device sealing and stability. Therefore, there is a considerable interest in developing solid-state or quasi solid state or gel polymer electrolytes (QSPEs) for EC devices. In this context, quasi solid or gel polymer electrolytes have received much attention due to their potential usage in many electrochemical applications including electro- chromic devices. Again, despite the many advantages of these gel electrolytes still there are some draw backs such as low ionic conductivity and low dimensional stability. A variety of QSPEs such as those formed by complexing a lithium salt with polyethylyneoxide (PEO), polyacronitrile (PAN) and natural polymers have been extensively studied during the last two decades [9,10]. Enhancement in the conductivity of these polymer electrolytes have been obtained by using plasticizers such as ethelene carbonate (EC) and propylene carbonate (PC).

By taking into account all the aforementioned factors and also our knowledge and experience on polymeric electrolyte we have focused our attention on the fabrication of a novel type of electrochemical device using TiO_2 as the electrochromic material and pure FTO as the counter electrode. A polymer gel electrolyte consisting of lithium chloride (LiCl), Ethylene Carbonate (EC), Propylene carbonate (PC) and Polyethylene Oxide (PEO) was used as the electrolyte medium. The ionic conductivity of the electrolyte was optimized by changing its composition while maintaining the gel nature of the electrolyte as much as possible. EC devices with the configuration FTO glass/TiO_2/EC:PC: LiCl:PEO electrolyte/FTO glass were fabricated and tested their electrochromic properties..

2. Materials and methods

2.1. Materials

Polyethylene Oxide (PEO) (Mw $\sim$ 120 000) purchased from Sigma Aldrich, propylene carbonate (PC), ethylene carbonate (EC), lithium chloride (LiCl) with purity >98% purchased from Fluka, Fluorine-doped SnO_2-layered (FTO) glass (sheet resistance 16 Ω/sq),) and transparent commercial TiO_2 paste purchased from Solaronix SA.

2.2. Working electrode

The electrochromic electrode of these ECD devices, usually a thin film of EC material, which can work either in the reflectance mode or in the transmissive mode, is constituted by a conductive transparent glass coated substrate. Many transition metal oxides exhibit EC properties. Among them TiO_2 was selected as the EC material due to its low cost and high abundance in nature. Electrochromic mesoporous TiO_2 films were prepared on fluorine-doped conducting tin oxide (FTO) glasses (sheet resistance $\sim$16 Ω/sq) by the "doctor blade" method using a TiO_2 paste and

then sintered at 450 $°C$ for 45 min. It should be mentioned that, it was not possible to obtain homogeneous and crack free films of TiO_2 with film thicknesses higher than 8.1 μm.

2.3. Counter electrode

The counter electrode can be of any material that provides a reversible electrochemical reaction in device operating in any mode (reflectance or transmissive). The charge that is used to colour the working electrode should store outside the working electrode to achieve bleaching. In most ECDs, ion storage films that operate in complementary redox mode to the active ECM are included as a counter electrode. In this study, FTO glass substrates (sheet resistance $\sim$16 Ω/ sq) were used as the counter electrode. Since there is no any additional coatings on the FTO substrate, preparation of counter electrode is cost effective.

2.4. Electrolyte

In order to find an electrolyte with highest ionic conductivity and suitable mechanical strength, different compositions of the electrolytes were synthesized using PEO, PC, EC and LiCl and their conductivity was measured using impedance spectroscopy. Room temperature ionic conductivity of the gel polymer electrolyte samples with different compositions were determined by a.c. impedance spectroscopy using a computer controlled Metrohm Autolab (PGATAT 128N) impedance analyzer in the frequency range of 0.1 Hz$-$10 MHz. For this, the polymer electrolyte was sandwiched between two polished stainless steel (SS) electrodes with the configuration SS/electrolyte/SS and measurements were taken. 0.3 g of ethylene carbonate, 0.3 g of propylene carbonate and 0.12 g of lithium chloride were added and dissolved completely. Then 0.1 g of Poly ethylene oxide (PEO) was added to this solution under continues stirring. The resulting viscous solution was used as the quasi solid (gel) electrolyte in the EC devices.

2.5. Fabrication of electrochromic device

The electrochromic device has five layers. The two outermost layers consist of glass coated with transparent electrical conductors such as Indium Tin Oxide (ITO) or Fluorine Doped Tin Oxide (FTO). One of the layers is coated with EC film and the other one is coated with ion storage film. A transparent ion conductor (electrolyte) is placed at the middle of these films, joining EC film and ion storage film which are physically separated, but ionically connected, by the liquid or solid (e.g., polymer) electrolyte.

In our study four layers device was fabricated instead of five layers. We have replaced the ion storage counter electrode by commercially available FTO and hence fabrication cost of the ion storage film was reduced. ECDs with configuration FTO glass/TiO_2/ polymer electrolyte /FTO glass and area of 2.1 $\times$ 1.5 cm^2 were fabricated as follows. A 1 mm thick spacer frame was placed on the TiO_2 electrode by keeping enough space for the electrical contacts from the FTO. Then the middle of the spacer frame was filled with the gel polymer electrolyte and sandwiched with the FTO counter electrode. The device was then sealed with a commercially available glue. The spacer was used to avoid the direct contact of the two electrodes. Typical structure of the ECD was given in the Fig. 1.

2.6. Characterization

The UV –visible optical spectra of the ECDs were recorded with a spectrophotometer in the wavelength range between 190 nm and 1100 nm. Cyclic voltammetry studies were carried out on TiO_2 films using a computer controlled Metrohm Autolab (PGATAT
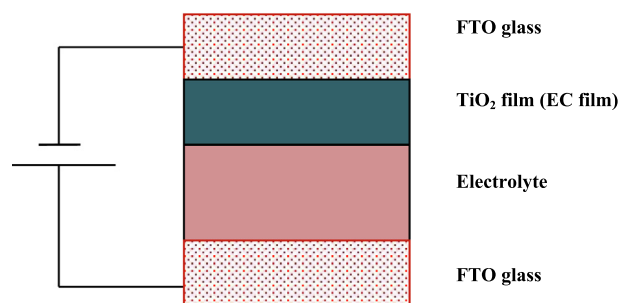
Fig. 1. Typical structure of electrochromic device with the configuration FTO glass/ TiO₂/polymer electrolyte /FTO glass.

128N) in the potential range from −2.0 V to +0.5 V with 10 mVs⁻¹scan rate.

3. Results and discussion

3.1. Electrolyte

The ionic conductivity was calculated using the relation $\sigma = l/R_b A$, where l is the thickness of the electrolyte sample, A is the contact area between the electrolyte and the electrode and the R_b is the measured resistance. This R_b value was determined by the intercept of the straight line with real axis of the Z'' Vs Z' Nyquist plot, Fig. 2. The ionic conductivity σ increases with the amount of salt and reach maximum of 1.28×10^{-3} Scm⁻¹ for a value of 0.3 g of EC, 0.3 g of PC and 0.12 g of LiCl. This is directly related with the increase in the number of mobile ions.

3.2. Electrochromic properties of TiO₂

Characterization of electrochemical properties of TiO₂ thin film as EC material was done by the cyclic voltammetry measurements. Fig. 3 shows cyclic voltammograms (CV) for the samples prepared. Electrochemical insertion and extraction was carried out using a solution of 1 M LiClO₄ in PC as the electrolyte with the platinum and the standard calomel electrode (SCE) as counter electrode and reference electrode respectively.

As can be seen from the figure, no cathodic peaks are observed in all the samples, however well-defined anodic peak is observed.
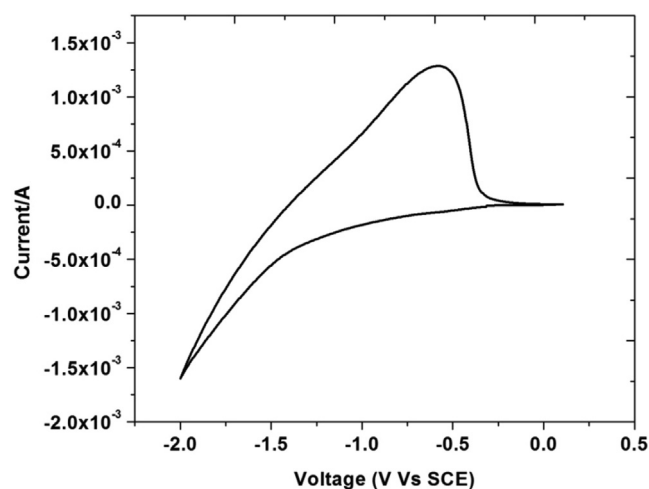

Fig. 3. Cyclic voltammetry of TiO₂/FTO films in 1 M LiClO₄ in PC (Scan rate 10 mVs⁻¹).

The position of anodic peak at −0.6 V is in good agreement with the literature data for anatase phase of TiO₂ [11].

As prepared TiO₂ thin film is a transparent one. The coloration of TiO₂ is a consequence of simultaneous insertion of electrons and Li ions to the TiO₂ film, leading to reduction of Ti⁺⁴ to Ti⁺³. On electrochemical reduction, Ti ⁺³ sites are generated to give the electrochromic effect turning its colour to blue. Since TiO₂ is a cathodically ion insertion material, in accordance with the following equation, the electrochromic process is the reversible insertion and extraction of the Li⁺ ions into/from the TiO₂ lattice [12,9]. The blue coloration of the film can be removed by the electrochemical oxidation.

$$Tio_2(transparent) + xLi^+ + xe^- \leftrightarrow Li_xTiO_2(deep\,blue) \qquad (1)$$
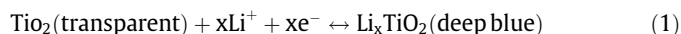
Accordingly, an application of a small curent/voltage to the TiO₂ electrolde, promotes the above reaction in the forward direction forming deep blue colored Li$_x$TiO₂. Cathodic polarization induces ion insertion and electron injection as indicated in the above equation. Inserted ions expands the TiO₂ lattice while the electrons modify its electronic band structure. Injected electrons can get
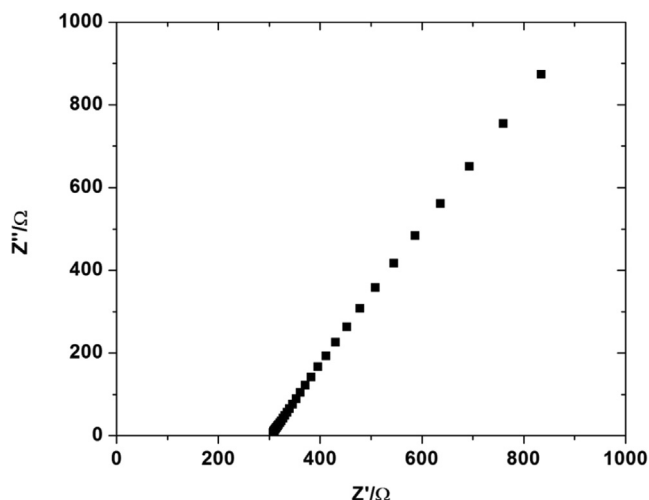

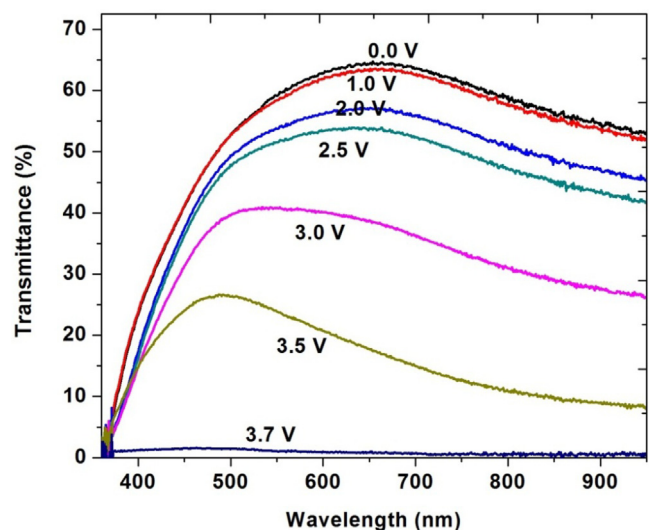**Fig. 2.** Complex impedance plot for the gel electrolyte with the configuration ss/Gel electrolyte/ss.

Fig. 4. Optical transmittance as a function of wavelength for the electrochromic device FTO/TiO₂/PEO electrolyte/FTO in various potential srages.

Table 1
Optical contrast and optical density of the ECDs with configuration FTO glass/TiO$_2$/polymer electrolyte(PEO) /FTO.

Cell	$T_{bleached}$ (s)	$T_{colored}$ (s)	ΔT(s)	ΔOD
FTO/TiO$_2$/PEO electrolyte/FTO	62.8	0.98	61.8	1.8
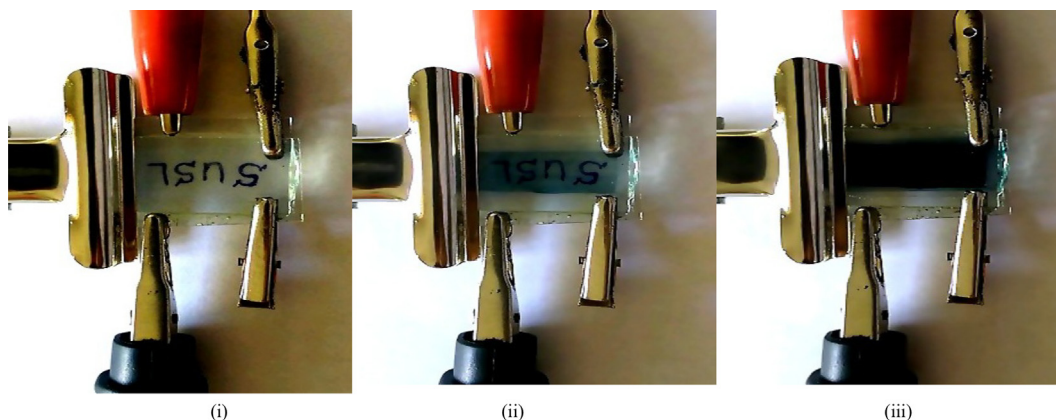
Fig. 5. Different electrochemical statues of the device FTO/TiO$_2$/PEO electrolyte/FTO (i) as prepared (ii) coloured (partially reduced) (iii) highly reduced.

trapped by a Ti^{+4} in TiO$_2$ forming Ti^{+3} and thereby modify the optical and electrical properties of the TiO$_2$ film. Therefore, the optical transmittance decreases as observed and reaches the minimum.

3.3. Electrochromic device

Electrochromic devices having the configuration FTO glass/TiO$_2$/polymer electrolyte (PEO) /FTO glass (Fig. 4) were subjected to coloration by applying an external potential between the two electrodes. The thickness of the transparent TiO$_2$ films was measured from the optical method. The calculated value of the film thickness was 8.1 μm.

Degree of coloration was varied by changing the applied potential. The electrolyte employed here is highly stabel and have not observed formation of any air bubble during the process at higher voltages confirming the stability of the electrolyte.

Fig. 4 shows the average transmittance of the ECD with the aforementioned configuration, at different status in the visible region when applying various potentials through the electrodes. Potential between two electrodes was increased gradually from 0.0 V to 3.7 V volts in 0.5 V steps. For each measurement the applied potential was kept constant at each value throughout the duration of the measurement (two min.) As can be seen from figure, ECDs fabricated with thin layers TiO$_2$ showed regular reduction of transmittance at each voltage steps. The reduction in the transmittance spectra at the wavelength of ~350 nm can be associated with the fundamental absorption edge.

The EC electrode prepared with 8.1 μm thick TiO$_2$ film showed around 0.9% transmittance at the colored state and the 63% at the bleached state. The variation of transmittance (optical contrast, ΔT %) and optical density (ΔOD) which refers to the light absorbing capability of the ECD were measured using the relations,

$$\Delta T = T_{bleached} - T_{coloured} \qquad (2)$$

$$\Delta OD = Log[T_{bleached}/T_{coloured}] \qquad (3)$$

where $T_{bleached}$ is the transmittance of the ECD in the bleached state and $T_{coloured}$ is the transmittance of the ECD in the coloured state.

61.8% optical contrast and 1.8 optical densities were observed for the ECD with 8.1 μm thickness (Table 1). Many reported TiO$_2$

based devices showed less optical contrast as compared with this device [12–17]. Relatively less transmittance difference between coloured and bleached states was reported by our group for the Electrochromic devices with the configuration FTO glass/TiO$_2$/polymer electrolyte (PMMA) /SnO$_2$/FTO glass [18,19]. High optical contrast for the device configuration FTO glass/TiO$_2$/polymer electrolyte (PEO) /FTO glass may be due to the improved ionic conductivity of the electrolyte. Possibility of using FTO as a counter electrode for the ECDs has confirmed through this study.

Fig. 5 shows the three different states of the ECD at different applied voltages (i) with zero voltage (bleached state), (ii) with 2.0 V (partially colored state) and (iii) with 3.7 V (fully colored state).

A double potential step chronoampherometry was perfomed in order to estimate the response time of the devices. Fig. 6 shows transmittance-time profile and the degree of coloration. Here the applied potential between two electrodes was changed from 0.0 V to 3.7 V. It can be clearly seen that the coloration time is 30 s.
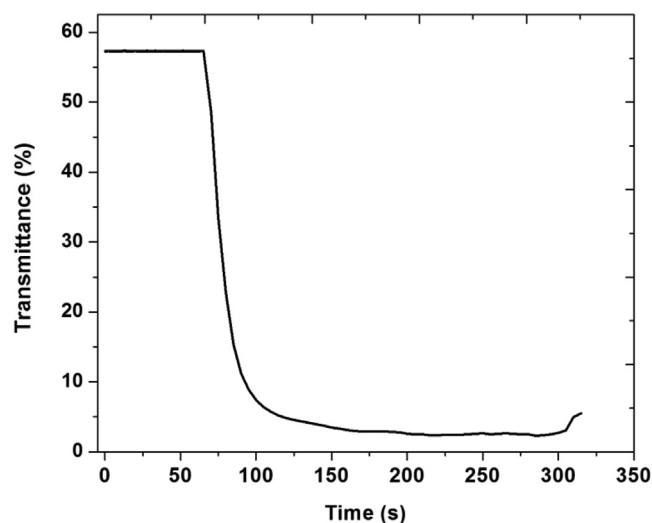
Fig. 6. Time taken to colored for the ECD with configuration FTO glass//TiO$_2$/polymer electrolyte (PEO) /FTO glass.
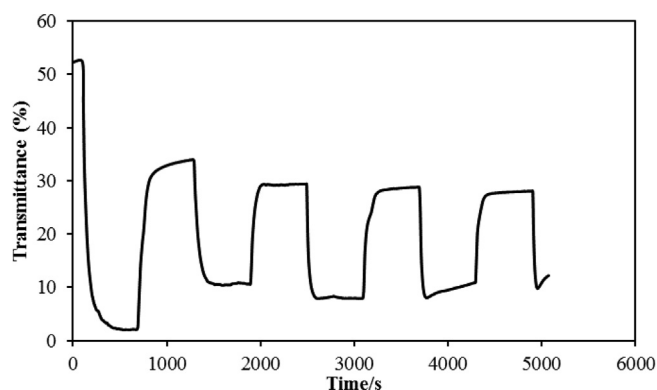
Fig. 7. Reversibility of the ECD with configuration FTO/TiO$_2$/polymer electrolyte (PEO)/FTO.

A double potential step chronoampherometry was performed to estimate the repeatability of the devices and its stability during the consecutive coloring bleaching steps. This test was performed by cycling the device between colored and bleached states. Here the applied potential between two electrodes was changed from −0.25 V to 3.0 V and the measurements were taken at the 1 s intervals for the coloration process. A negative potential (−0.25 V) was appied during the every bleaching process. Following figure (Fig. 7) shows the kinetics of the transmittance variation measured at λ = 600 nm. As can be seen in Fig. 7, reversible process of colouring and bleaching according to the applied step potential has sustained. The stability of the device changes within the first cycle and then it remains constant.

4. Conclusion

In order to explore the possibility of replacing expensive oxide semiconductor electrodes in electrochromic devices, readily available, low cost TiO$_2$ and FTO were employed in the fabrication of ECDs and tested their performances with PEO based polymeric electrolyte comprising Li$^+$ ions. A reversible color change between dark blue and colorless states was observed when an appropriate voltage (3.7 V) was applied repeatedly to the electrochromic device.

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