COMPLEMENTARY ELECTROCHROMIC DISPLAY SYSTEM BASED ON PRUSSIAN BLUE THIN FILM

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Abstract: *An approach based on thin film/solution type Electrochromic System is described here wherein coloration from blue to colorless is realized under applied DC voltage pulse. Iron (III) hexacyanoferrate (II) is more commonly known as Prussian blue and shows intense blue color due to inter valence electron transports. Thin film of PB is developed on ITO by the electrochemical reduction of solution containing iron (III) and hexacyanoferrate (III) ions. Further, the two step reduction process in PB/Organic ionic system shows reversible electrochromism. The first step involves one electron reduction of Prussian blue at -1 volt. In the second stage further one electron reduction of thin film of PB is realized at -1.5 volt. In this system, blue(PB) to colorless (PW) state is realized while analyzing the reversibility of the process through Cyclic voltametry recorded with PG/ECIS (ECO CHEMIE model Autolab 30) system in between 0.0 to -1.5 V. The reduction peaks are seen at -1 V and at - 1.5 V, respectively. It was observed that such complementary EC system is more effective in showing the reversible electrochromism with faster switching response. Coloration and discoloration process is analyzed by recording transient current characteristics under pulse mode biasing maintaining the pulse timing of 50 Seconds. Parameters like electrochromic contrast (Δ%T) and coloration efficiency (η) have been evaluated at different biasing.*

Keywords: Electrochromic; contrast; Reduction; Coloration; Prussian Blue

Introduction

An electrochromic material is one where a reversible color change takes place upon reduction (gain of electrons) or oxidation (loss of electrons), on passage of electrical current after the application of an appropriate electrode potential. The complementary electrochromic system has been found to be more effective in achieving better coloration efficiency in comparison to other conventional system wherein only solid state or electrochemical approach is adopted.

Generally, complementary electrochromic devices can be categorized in three type (i) Solution type (ii) Precipitation type (iii) Thin film type [1]. The first type includes materials with at least one colored and one bleached state. These materials are especially useful for absorption/transmission type device applications such as smart windows and optical shutters e.g. Metal-oxides, organic electrochromes and polymers. Second class of materials consists of electrochromes with two distinct colored states. These EC materials lack a transmissive state but are useful for display type applications where different colors are desired in different redox states e.g. Polythiophene based EC system is the best example of this, where switch from red to blue takes place upon oxidation. A third class of materials includes EC materials where more than two colors are accessible depending upon the redox states of the materials e.g. Conjugated polymers due to their versatility for making blends, laminates and copolymers.

In the present work, we have described a PB system wherein one electron reduction process is observed at two stages i.e. at -1.0V and second at -1.5V, respectively. Initially, the fabricated panel of the size 4" X 4" was having base blue color of PB and that after successive biasing becomes completely colorless. The same process is explained by analyzing its optical spectral and electrical properties and applied voltage pulse.

Experimental details

Fabrication of 4" X 4" Panel: The PB film was grown over indium tin oxide coated glass substrate by simple electrolysis process. In the process, the 0.01M of $FeCl_3$ solution was taken in a beaker and then 0.1M KCl and 0.1M HCl were added stepwise with constant stirring. Further, $K_4Fe(CN)_6$ 0.01 M was added into the reaction constant. Electrolysis was carried out at 2.5 V for 15 minutes leading to the formation of very smooth film of PB which is placed exactly parallel to another SnO_2 (fluoride doped) coated glass substrate. The supporting electrolyte is placed in between two plates and electrical contact is made through silver paste. The ready panel formed in this way was able to show complementary reversible electrochromism.

Optical Characteristics Optical transmittance and absorption characteristics were recorded particularly in the form of thin film by PDA Spectrophotometer (ANALYTIC JENA) before and after biasing at 0 to2.2 volt (Fig1.)

Cyclic Voltametry: Cyclic voltametry of Prussian blue film/solution based complementary EC system (Fig.2) was recorded by potentiogalvenostat (Autolab 30). Oxidation and reduction peaks were recorded at +1 to -1 voltage range. Step potential and scan rate was 0.050V and 0.069V/s, respectively.

Current-Voltage characteristics

I-V Characteristics of Prussian blue film was recorded by potentiogalvenostat (Fig.3)) from 0 to 2.5 volt. It shows diode like behavior from 1.5 onwards. Transient current behavior was also recorded (Fig. 4) in pulse mode biasing with the help of Oscilloscope (TDS 2024).

Results & Discussion

The transmittance characteristics recoded with and without biasing (Fig. 1) show about 25 percent change covering almost entire visible region under the biasing of 2.2V. The electrochromic contrast which is the most important factor in evaluating an electrochromic system and often reported as a percent transmittance change (Δ%T) at a specific wavelength 635nm where the EC material has the highest optical contrast. The evaluated (Δ%T) was found to be 12 in this complementary system.

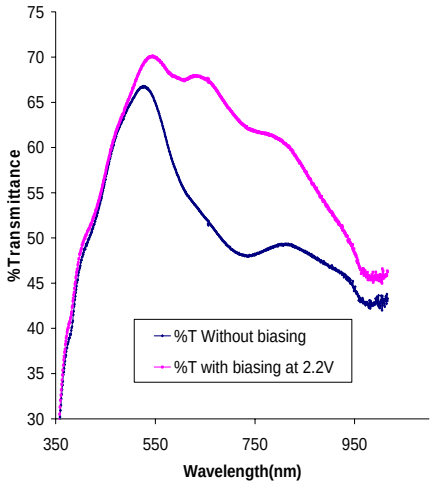

Figure1. Optical Transmittance

The coloration efficiency considered as practical tool to measure the power requirements of an electrochromic material [2-3] was also evaluated by determining the amount of optical density change (ΔOD) induced as a function of the injected/ejected electronic charge (Q_d), i.e. the amount of charge necessary to produce the optical change given by the equation

$$\eta = (\Delta OD) / Q_d = \log [Tb/Tc] / Q_d$$

where η (cm^2/C) is the coloration efficiency was found to be 94.8 at a given λ of 635nm and Tb and Tc are the bleached and colored transmittance values, respectively.

Cyclic voltammogram recoded for PB based film/solution complementary system (Fig. 2) shows very distinct oxidation and reduction peak. Oxidation peak appears at 0.36V and respective reduction peak is seen at -0.1 V. The complete EC system governs by one electron reduction process induced by DC pulse showing coloration to discoloration.

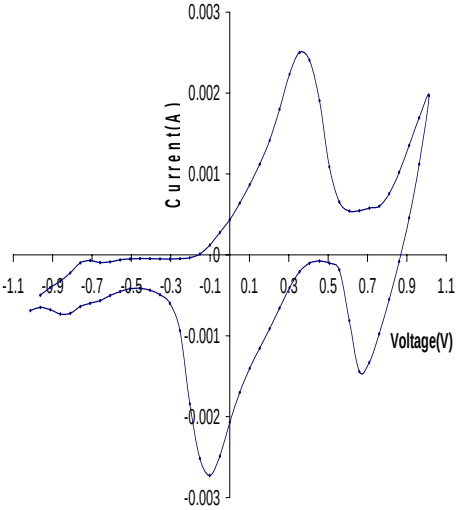

Figure2. Cyclic-Voltammogram of PB thin film/ solution complementary system

The Current-voltage characteristics recorded for this panel shows a sharp change in current in between 1.5V to 2.3 V DC biasing. This shows that the given biasing imparts oxidation-reduction process wherein one electron reduction of PB film leads to the formation of transparent PW. It is a reversible process and after removing the biasing it comes back to original PB state.

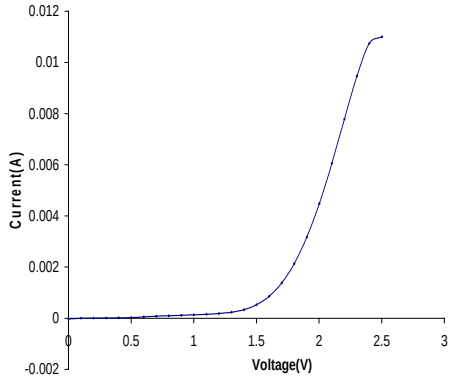

Figure 3. Current-Voltage characteristics

Transient current of the device recorded in pulse mode biasing with pulse amplitude of 2.2 volt (Fig.4). Maximum transient current of 8mA was observed while the steady state current was less than 1mA. Being capacitive device it takes initially high transient current and after complete charging of the matrix, further requirement of current reduces to a great extent showing steady current of 1mA.

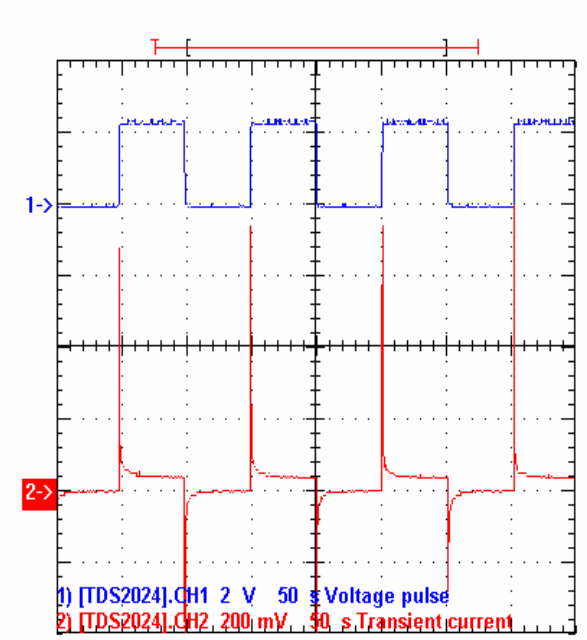

Figure 4. Transient Characteristics

Conclusion:

The proposed complementary EC system reveals effective coloration to discoloration electrochromic phenomenon as evidenced by its optical and electrical characteristics recorded under DC pulse. The observation verifies the reversible one electron reduction of PB leading to the formation of PW at 2.2V biasing. The removing of potentials leads to original blue colored PB state. The evaluated electrochromic contrast (Δ%T) =12 and coloration efficiency η =94.8 cm^2/C along with switching response of few seconds supports its possible application in electrochromic window.

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