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Electrochromic Properties of Prussian Blue Thin Films Prepared by Chemical Deposition Method

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Abstract

The manifestation of electrochromic phenomena makes Prussian blue (PB) thin films very attractive, especially because they exhibit four-color polyelectrochromicity. In this work PB thin films were prepared by simple and low cost shemical deposition method. The films were deposited onto fluorine doped tin oxide (FTO) coated glass substrates. An electrochromic test device (ECTD) was constructed by using these films as working electrodes, and FTO coated glass as an opposite electrode in aqueous solution of 1 mol/dm^3 KCl as supporting electrolyte. The electrochemical properties of the films were characterized by cyclic voltammetry. The obtained films exhibited electrochromism, changing color from deep blue in as deposited state into green, and back to blue and colorless. Visible transmittance spectra of PB films were studied in-situ in as deposited, colored and bleached states. From those spectra, contrast ratio (*CR*) and the optical band gaps E_g were evaluated. The dependence of the optical density (*OD*) on charge density was examined and the coloration efficiency (*CE*) was calculated to be 149.8 cm^{2}C^{-1}. The time response during the film switching between transparent and blue states was also examined.

Keywords: Chemical deposition; Electrochromism; Prussian blue; Thin films.

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1. Introduction

The ability of certain materials to change reversibly their properties (transmittance, reflectance and absorbance) under an applied voltage is called electrochromism [1, 2]. Since its discovery [3], electrochromism has been an area of active research interest and considerable progress has been achieved in the syntheses and application of electrochromic materials, the improvements of electrochromic properties and the fabrications of electrochromic devices. Today electrochromic materials have many interesting technological applications, such as smart windows, antiglare mirrors, displays and camouflages [2-6].

Traditionally, materials have been considered as being electrochromic when they displayed distinct visible color changes, with the color change commonly being between a transparent (bleached) and a colored states, or between two colored states. In cases where more than two red-ox states are electrochemically available, the electrochromic material may exhibit several colors and be described as polyelectrochromic. Many inorganic and organic materials exhibit electrochromic properties. Common inorganic electrochromic materials are transition metal oxides and metal hexacyanometallates, while viologens, phthalocyanines, conducting polymers and metallopolymers are common organic and polymer electrochromic materials [7].

Prussian blue [PB, iron (III) hexacyanoferrate (II)] was produced for the first time in Berlin by Diesbach [8]. It is a prototype of a number of polynuclear transition metal hexacyanometallates which forms an important class of insoluble mixed valence compounds with a general formula $\mathrm{M'_i}\left[\mathrm{M''(CN)_6}\right]_k$ where *i* and *k* are integers, and $\mathrm{M'}$ and $\mathrm{M''}$ are transition metals with different formal oxidation numbers. In the case of PB, $\mathrm{M'}$ and $\mathrm{M''}$ are iron ions with oxidation states $\mathrm{Fe^{III}}$ and $\mathrm{Fe^{II}}$. Although, as an important inorganic pigment, PB has been extensively used as a pigment in paints, printing inks and other color uses, not much was known about its electrochemistry. This might be due to the lack of knowledge for the preparation of PB in the form of thin films.

Prussian blue films that can be switched to green and colorless red-ox states were first reported by Neff [9] in 1978. Since then, PB films have raised intense interest not only because of their electrochromic, but also because of their ion-exchange, ion-sensing, electrocatalytic and photomagnetic properties [10].

PB films exhibit four-color polyelectrochromicity [11, 12]. It was found [13] that PB thin films may be:

Reduced to Prussian white – PW (also known as Everitt’s salt), which appears transparent as a thin film:

$$\underset{\mathrm{PB}}{\left[\mathrm{Fe^{III}Fe^{II}(CN)_6}\right]^-} + \mathrm{e^-} \rightarrow \underset{\mathrm{PW}}{\left[\mathrm{Fe^{II}Fe^{II}(CN)_6}\right]^{2-}} \qquad (1)$$

Partly oxidized to Prussian green – PG (also known as Berlin green):

$$\underset{\mathrm{PB}}{\left[\mathrm{Fe^{III}Fe^{II}(CN)_6}\right]^-} \rightarrow \underset{\mathrm{PG}}{\mathrm{Fe^{III}}\left\{\left[\mathrm{Fe^{III}(CN)_6}\right]_{2/3}\left[\mathrm{Fe^{II}(CN)_6}\right]_{1/3}\right\}^{1/3-}} + \frac{2}{3}\mathrm{e^-} \qquad (2)$$

Wholly oxidized to Prussian brown – PX (actually yellow in thin-film form):

$$\underset{\text{PB}}{\left[\mathrm{Fe^{III}Fe^{II}(CN)_6}\right]^-} \rightarrow \underset{\text{PX}}{\left[\mathrm{Fe^{III}Fe^{III}(CN)_6}\right]^0} + \mathrm{e^-} \qquad (3)$$

Prussian blue is anodic coloring electrochromic material which becomes colored under charge extraction [14]. Its application in electrochromic devices is mainly based on switching between PW and PB. The final product of the oxidation process – Prussian yellow, is slightly soluble and therefore unsuitable for an application.

Several methods have been known for the preparation of electrochromic PB thin films, mostly with electrochemical deposition [9, 11, 14-16] although an electroless deposition [17] and sacrificial anode [18] method have been described also. The composition of PB thin films is extraordinarily preparation sensitive, so the deposition method has a crucial role in their electrochromic behavior.

The aim of this work is to investigate the electrochromic properties of PB films prepared by recently developed simple chemical deposition method [19].

2. Materials and methods

2.1. Chemicals and accessories

Aqueous solutions of 0.1 mol/dm^3 $Fe_2(SO_4)_3$; 0.1 mol/dm^3 $K_4[Fe(CN)_6]$; 3 mol/dm^3 HCl; 1 mol/dm^3 KCl with 2 drops of conc. HCl in 100 ml. FTO coated glass substrates with transparency of about 80% for visible light and sheet resistance of about 15Ω/□. The reagents were produced by Merck and supplied by Biotek, Skopje. All solutions are prepared from analytical grade reagents and used without purification.

2.2. Preparation of PB films

Electrochromic PB films were easily prepared by chemical deposition which was performed from two solutions. One of the solutions was prepared by mixing of 15 ml 0.1 mol/dm^3 $Fe_2(SO_4)_3$, 90 ml H_2O, 0.5g ethylenediaminetetraacete (EDTA) and 10 ml 3 mol/dm^3 HCl in 250 ml beaker, while the second solution was an aqueous solution of 15 ml 0.1 mol/dm^3 $K_4[Fe(CN)_6]$, 90 ml H_2O and 10 ml 3 mol/dm^3 HCl in 250 ml beaker. Before the deposition, the solutions were heated up to 60^0 C. The films were produced by successive immersion of the substrates into the solutions. The detailed description of the deposition procedure is given in [19]. The thickness of the films depends on the number of the cycles. The films investigated in this work were deposited by 20 cycles. The thickness of the films, measured by Dectak Stylus Profilometer, was 140 nm.

2.3. Characterization

The electrochemical properties of electrochromic PB thin films were characterized by cyclic voltammetry measurements. The Cyclic voltammetry was performed using Micro AUTOLAB II equipment (Eco-Chemie, Utreht, Netherlands) in one compartment three electrodes electrochemical cell, with PB film as working electrode, platinum wire as counter electrode and saturated calomel electrode (SCE) as reference electrode. The cycling was carried out within a potential rang from -0.2 V to +1.2 V and back to -0.2 V in 1 mol/dm^3 KCl aqueous solution (slightly acidified with 2 drops of conc. HCl in 100 ml) as an electrolyte. The voltage scan rate was 10 mV/s, and the film working area was 1 cm^2.

For practical electrochromic investigations, an electrochromic test device (ECTD) was designed [20-22]. It consisted of home-built glass cell with a 1mol/dm^3 KCl (slightly acidified with 2 drops of conc. HCl in 100 ml of the solution) as an electrolyte, in which two electrodes were immersed. One electrode was PB thin film deposited on FTO substrate (working electrode) and the other was blank FTO substrate (counter electrode). The distance between the electrodes was about 1.5 cm, and the volume of the electrolyte was about 20 ml. The active surface area of the electrodes was approximately 6 cm^2. Figure 1 depicts the cross section of the so – designed ECTD.

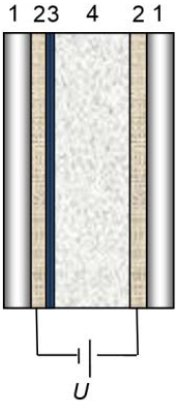

Figure 1: Cross-section of the ECTD: 1- glass, 2 – FTO, 3 – PB film, 4 – electrolyte.

The optical properties of the PB films were investigated using Varian CARY 50 Scan UV-Visible spectrophotometer, in the wavelength range from 300 to 900 nm. The visible transmission spectra were taken in-situ (The PB film incorporated as a working electrode into the ECTD). An electrochromic cell with two clean FTO substrates filled with electrolyte was measured as 100% background. The bleaching and coloration of the PB thin films were performed with applied voltages of -2 V, -1 V, and +2 V.

The visible transmittance spectra were used for calculations of contrast ratio $CR(\lambda)$ of the PB films. Contrast ratio is a parameter that quantifies the intensity change between the different color states, and can be calculated by equation [23]:

$$CR = \frac{T_b(\lambda)}{T_c(\lambda)} \tag{4}$$

where $T_b(\lambda)$ and $T_c(\lambda)$ are the transmittance data (at a particular wavelength) of the PB film in its bleached and colored states respectively. Usually, $CR(\lambda)$ is calculated at a specific wavelength where the films have the higest optical contrast.

From the transmittance data (T) and the film tickness (t = 140 nm) the absorption coeficient was determined using the equation:

$$\alpha = \frac{1}{t}\ln\frac{1}{T} \tag{5}$$

The optical band gaps E_g of the PB film in as deposited, bleached, blue and green states were evaluated from the standard expression [24, 25]:

$$\alpha h\nu \propto \left(h\nu - E_g\right)^m \tag{6}$$

where $h\nu$ is the energy of the incident photon, E_g is the optical energy gap, and m is the number which characterizes the optical processes. The value of m is $1/2$ for direct allowed transition, $3/2$ for direct forbiden transition, and 2 for indirect allowed transition. When the straight portion of the graph $(\alpha h\nu)^m$ against $h\nu$ is extrapolated to $\alpha = 0$, the intercept gives the transition band gaps.

An important parameter for the caracterization of the electrochromic films is the coloration efficiency $CE(\lambda)$ which represents the change in the optical density (ΔOD) per unit charge density change $(\Delta Q/S)$ during coloration [26] and can be calculated by the equations:

$$CE(\lambda) = S\frac{\Delta OD}{\Delta Q} \tag{7}$$

and

$$\Delta OD = \log\frac{T_b(\lambda)}{T_c(\lambda)} \tag{8}$$

where $T_b(\lambda)$ and $T_c(\lambda)$ are the transmittance data of the bleached and colored states respectively, ΔQ is the change of the injected/ejected charge, and S is the active area of the electrochromic film. The ideal electrochromic material would show a high transmittance change by applying low charge to get large CE.

In this work, the coloration efficiency was calculated from (ΔOD) at given wavelength of 700 nm, and $(\Delta Q/S)$ during the coloration, after films were fully bleached. The ejected charge was determined by the applied constant current and the time of its application.

The time taken for an electrochromic material to switch between its colored and bleached states is known as response time. The responsivness of the film was examined in situ at 550 nm (white light) as a transmittance change due to abrupt voltage change between -2 V and -1 V.

3. Results and Discussion

PB films investigated in this work exhibited good electrochromic properties. The X-ray diffraction (XRD) patterns of the relatively thick PB film showed that the deposited material is amorphous [19]. The films had deep blue color (optical transmittance of 47% for visible light) in as deposited state, and changed the color from blue to green at +2 V, from green to blue at -1 V, and became transparent at -2 V.

Figure 2 presents photographs of PB film in: A) as deposited, B) green (+2V), C) blue (-1V) and D) transparent (-2V) states. The photographs is made ex-situ, so that the sample was first bleached (colored) in the ECTD and than removed from the ECTD, rinsed in distilled water, dried, and than photographed. From these photographs one could clearly notice the different colors of the film.

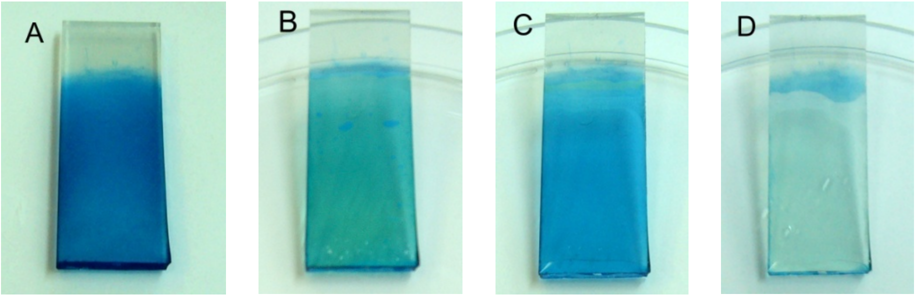

Figure 2: Ex-situ photographs of chemically deposited PB thin films in: A) as-deposited, B) green, C) blue and D) transparent states.

The electrochemical properties of electrochromic PB thin films were characterized by cyclic voltammetry (CV) measurements. In Fig. 3 are presented five cyclic voltammograms of the PB thin film. One could see that all voltammograms have a same shape, which means that the films exibited good stability. The voltammograms also show two reduction and two oxidation peaks, meaning that the system in both cases is composed of two relatively stable red-ox couples. The oxidation peak i_{ap1} at 0.211 V and the reduction peak i_{cp1} at 0.180 V are due to PB-PW red-ox switch. Bleaching process is followed by reduction of Fe^{III} ions and intercalation of potassium ions:

$$\mathrm{KFe^{III}\left[Fe^{II}(CN)_6\right] + e^- + K^+ \rightarrow K_2Fe^{II}\left[Fe^{II}(CN)_6\right]}$$

The coloration is followed by the opposite process, deintercalation of ions.

The oxidation peak i_{ap2} at 0.944 V is due to the partial oxidation of PB to PG. This process is followed by partially oxidation of Fe^{II} ions:

$$\mathrm{\left\{KFe^{III}\left[Fe^{II}(CN)_6\right]\right\}_3 - 2e^- - 2K^+ \rightarrow \left\{Fe^{III}\left[Fe^{III}(CN)_6\right]\right\}_2\left\{KFe^{III}\left[Fe^{II}(CN)_6\right]\right\}}$$

and the reduction peak i_{cp2} at 0.896 V is due to the reverse process [13]. The experimental values for voltammogram charge, peak current, peak potential and half-peak width are given in Table 1. According to the results for Q^+/Q^- (Q^+ is the coloration charge and Q^- is the bleaching charge) and i_{ap}/i_{cp} (i_{ap} is the anodic peak current, whereas i_{cp} is the cathodic peak current), the values are close to unity, which means that PB thin films exhibited excellent reversibility. The deviations from the teoretical value are in the range of the experimental error.

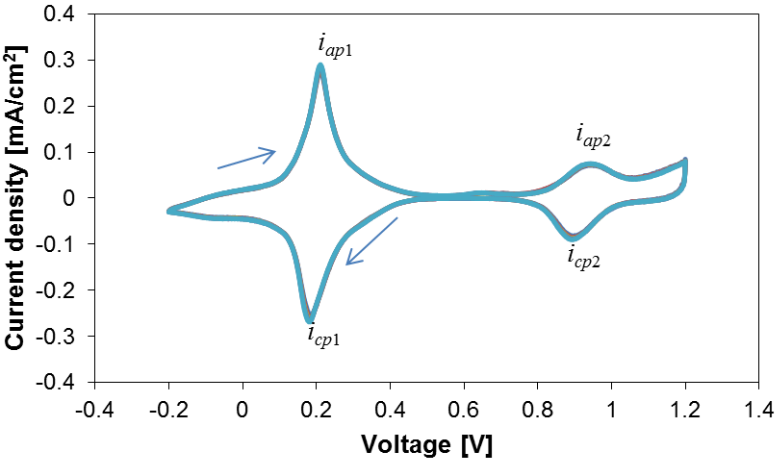

Figure 3: Cyclic voltammogram (five cycles) at 10 mV/s scan rate for chemically deposited PB thin film in 1 mol/dm^3 KCl aqueous solution. Arrows indicate direction of potential scan.

Table 1: CV parameters of chemically deposited PB thin films

Q^+ (C)	Q^- (C)	Q^+/Q^-	i_{ap} (mA)	i_{cp} (mA)	i_{ap}/i_{cp}	E_{ap} (V)	E_{cp} (V)	$W_{ap1/2}$ (V)	$W_{cp1/2}$ (V)
0.0060	0.0058	1.034	0.2582	-0.2523	1.023	0.211	0.180	0.0697	0.0709
0.00101	0.00097	1.041	0.0646	-0.0699	0.924	0.944	0.894	0.1395	0.1162

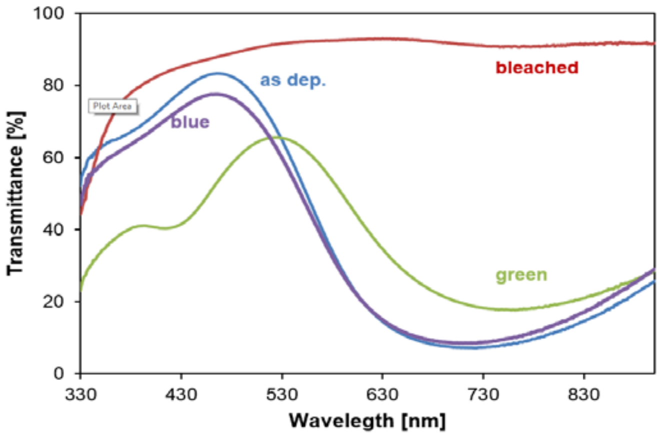

Figure 4: In-situ visible transmittance spectra of chemically deposited PB thin film in as deposited, green blue and transparent states.

The transmission spectra of the film, in the wavelength range from 300 to 900 nm, in: as deposited, bleached and colored state, all taken in-situ, are presented in Fig. 4. The contrast ratio of the PB film between the transparent and the blue states (a), as well as between the transparent and the green states, in the same wavelength range, calculated by equation (4), is presented in Fig. 5. As it can be seen from Figs. 4 and 5, the maximum transmittance change (of about 84 %) and the highest *CR* (~11) between transparent and blue states occurs at 700 nm, while the maximum transmittance change (of about 73%) and the highest *CR* (~5) between transparent and green states occurs at 760 nm.

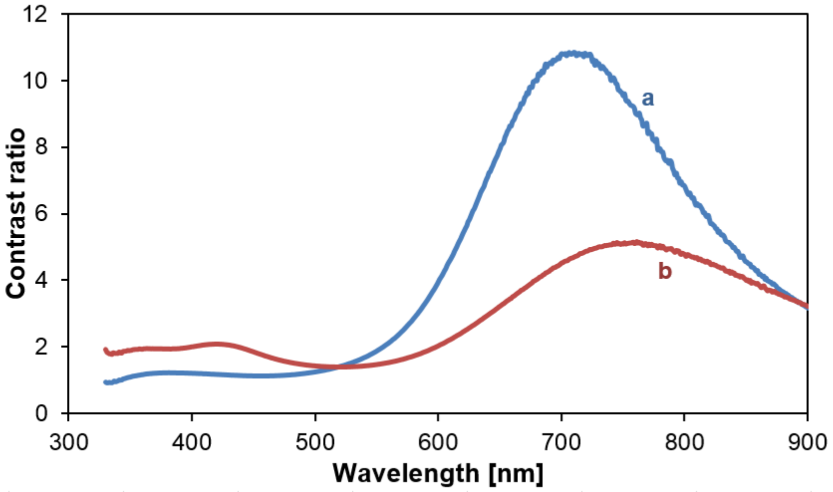

Figure 5: Contrast ratio of the PB film between its transparent and blue states (a), and transparent and green states (b), versus wavelength.

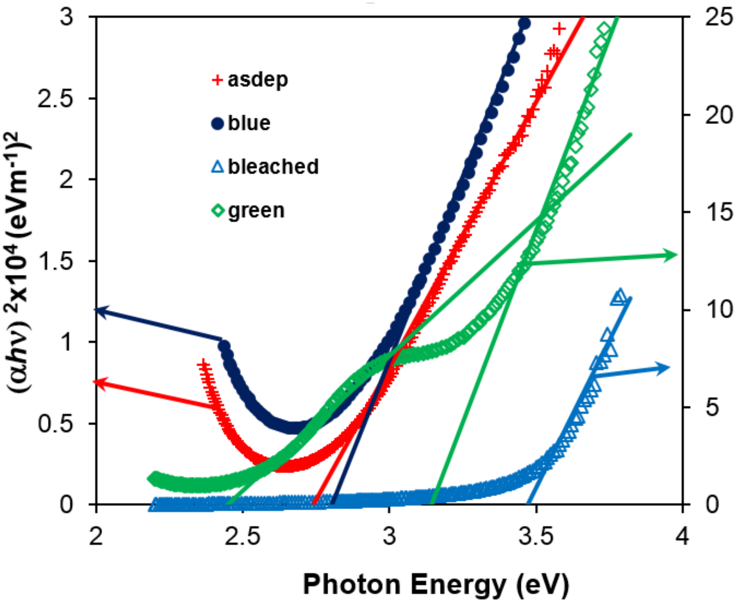

Figure 6: Plots of $(\alpha h\nu)^2$ as a function of photon energy $(h\nu)$ for chemically deposited PB thin film in as deposited, green, blue, and transparent states.

Utilizing the transmittance data and the film thickness, the band gaps E_g of the as deposited, green, blue, and transparent states were evaluated. Figure 6 shows the plot of $(\alpha h\nu)^2$ versus the photon energy $(h\nu)$ for all, as deposited, transparent, blue, and green states. The linear trend in this presentation (the linear dependence) shows a presence of direct electron transition mechanism for all states of the film. The band gaps were calculated from the linear parts in Figure 6, as intercepts with the photon energy axis. The obtained results for optical band gaps of the four different film states together with the correlation coefficients are given in Table 2.

The presence of two band gaps for green state could be ascribed to coexistence of both, PB (2.45 eV) and PX (3.14 eV), as it is suggested in equation *(2)*. Similar results are reported in [27] for theoretically calculated optical band gaps using density of states (DOS) calculations.

Table 2: The band gap E_g evaluated from Figure 6

State	E_g (eV)	R
As deposited	2.74	0.9969
Green	3.14; 2.45	0.9607; 0.9914
Blue	2.79	0.9975
Transparent	3.48	0.9731

Figure 7 presents the graphical presentation of the optical density charge (ΔOD) as a function of a charge density change $(\Delta Q/S)$. The *CE* at 700 nm was extracted as the slope of the line fitted to the linear region of the curve. The calculated *CE* value was found to be 149.8 cm^2/C (with the correlation coefficient R = 0.9975), which is a good value compared with the reported values in [16, 28, 29].

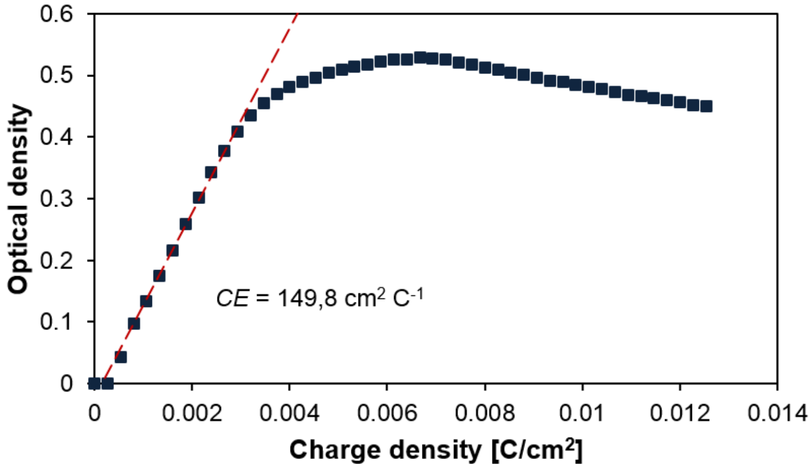

Figure 7: The dependence of the optical density on the charge density at 700 nm

In order to examine the time response (coloration and bleaching times), the transmittance at 550 nm (white light) was measured in situ through the ECTD. The applied potential was switched between – 2 V (transparent state) and – 1 V (blue state). Figure 8 presents the time response of the transmittance at 550 nm during the film switching between transparent and blue states. The bleaching and the coloration times, defined as time to reach 2/3 of the final change [21, 30] were found to be 12.5 and 1.7 s respectively. To preserve the electroneutrality of the solid electrochromic film, potassium ion uptake/loss must accompany the color transfer [29]. The difference in switching times is likely to relate to different rates of ingress/egress of potassium ions in the film.

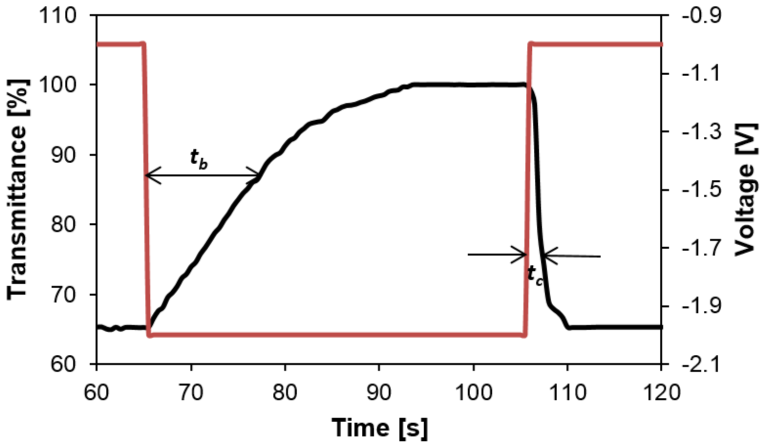

Figure 8: The time response of the transmittance at 550 nm during one cycle of bleaching and coloring. The applied potential was switched between -2 V and -1 V

4. Conclusions

Prussian blue thin films investigated in this work were deposited onto FTO coated glass substrates by chemical deposition method. The method is simple, economical, and offers a possibility for large area depositions. The chemicals were available and relatively cheap. The obtained films exhibited good electrochromic properties. They were stable and exhibited excellent reversibility, with color changed from originally deep blue into green, and back to blue and colorless. The optical and electrochromic properties of the films are convenient for visible light intensity modulation applications. The maximum difference in the transmittance and the highest contrast ratio between the blue and transparent states was found to be 84% and 11 respectively, at 700 nm, and 73% and 5 respectively, at 760 nm between the green and transparent states. Band gaps were evaluated from transmittance measurements for the four film states: as deposited, green, blue, and transparent assuming a direct semiconductor transition mechanism. The coloration efficiency (at 700 nm) was found to be 149.8 cm^2/C, which is a good value compared with those reported for the PB films obtained by electrochemical deposition method. The switching times between the transparent and blue states of the film were found to be 12.5 s for bleaching and 1.7 for coloring. The difference in switching times is likely to relate to different rates of ingress/egress of potassium ions in the film. Finally we can conclude that Prussian blue thin films obtained by chemical deposition method could be very promising materials for applications in electrochromic devices.

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