American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS)

ISSN (Print) 2313-4410, ISSN (Online) 2313-4402

http://asrjetsjournal.org/

Energy Efficiency with Electrochromic Prussian Blue Thin Films

I. Aliji[a,b]*, J. Velevska[b], M. Najdoski[c]

[a]*Faculty of Natural Sciences and Mathematics, Tetovo State University, Ilinden bb, Tetovo 1200, Republic of Macedonia*

[b]*Institute of Physics, Faculty of Natural Sciences and Mathematics, Sts Cyril and Methodius University, Arhimedova 3, Skopje 100, Republic of Macedonia*

[c]*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Sts Cyril and Methodius University, Arhimedova 5, Skopje 100, Republic of Macedonia*

[a]*Email: isak.aliu@hotmail.com*

Abstract

Prussian Blue (PB) thin films were prepared by chemical bath deposition onto fluorine doped tin oxide (FTO) coated glass substrates. Elelctrochromic behavior of the films was examined in an electrochromic device (ECD) consisted of home-built glass cell with a 1 mol/dm3 KCl as an electrolyte, PB film as working, and FTO as counter electrodes. These films showed electrochromism changing color from deep blue in as deposited state, to green in oxidized state, and back to blue and transparent (colorless) in reduced state. Visible transmittance spectra of the PB thin films in bleached and colored states were recorded in-situ. Absorption coefficients spectra were calculated using the transmittance spectra. The output integral of the spectral intensity and the integral of the spectral modulation were calculated by taking the solar irradiance spectrum AM 1.5 for a normal illumination on a PB – based ECD, and the absorption coefficients spectra of the PB films in their bleached and colored states.

Keywords: Electrochromism; Prussian Blue; Thin films; Energy efficiency; Solar light modulation.

1. Introduction

One of the biggest challenges of the present century throughout the world is environment protection. In order to protect our environment, we have to reduce our energy consumption.

---

* Corresponding author.

Buildings, consuming more than one third of the overall energy worldwide, have more impact on environment than industry and transportation. This is the reason why, the energy consumption reduction in the buildings is a big challenge for every country in the world, especially countries with large climate and temperature variations [1].

Over the last years buildings design has been oriented toward the energy usage, the protection of the environment and the occupants' comfort [2]. On the other hand, modern urban architecture involves the construction of large buildings with a big percentage of glazed areas. Glass is ubiquitous in buildings because of the positive impact that natural daylight and the connection with outdoors have on people's health and well-being. Despite these desirable benefits, windows are also the greatest cause of thermal and visual discomfort in buildings. Since glazing constitutes one of the less energy efficient components of the building envelope, the window choice has a huge impact on the reduction of building energy consumption. The control of incident solar radiation through the windows is a key element for the achievement of indoor comfort and more generally of greater energy efficiency in buildings.

The increasing attention to issues of visual comfort and energy efficiency that characterized the architecture of the twenty first century led to the development of innovative dynamic glazing technologies, aimed not only at reducing heat loss, but also at controlling incoming solar radiation, in order to maximize the solar gain in winter and minimize it in summer, as well as ensuring the best natural lightening conditions with no glare [3]. Among these technologies is electrochromic glazing (smart windows), that manage solar radiation flux entering buildings by controlling the glazing opacity [4]. In this manner, smart windows offer increased thermal and visual comfort, daylight control and energy savings without loss of view. With an electrochromic glazing, architects can for the first time design larger areas of glass into the building envelope to capitalize on the beneficial aspects of the sun while at the same time minimizing its negative effects [5].

Crucial role in electrochromic windows have a special materials that have electrochromic properties. "Electrochromic" describes materials that can change their optical properties (color) by applying small voltage. The classification of the electrochromic materials is related to the potential at which the coloration process occurs. Materials with anodic coloration exhibit coloration at positive potential (charge extraction), while materials with catodic coloration exhibit coloration at negative potential (charge insertion). When thin films of such materials are integrated in devices, it becomes possible to modulate the transmittance, absorptance, reflectance and emittance between widely separated extrema. A standard electrochromic design consists of a substrate coated with transparent conductor, an electrochromic coating, an electrolyte and a counter electrode. A voltage applied between the transparent conductors causes the ions from the electrolyte to be injected into the electrochromic film (cathodic material), or extracted from the electrochromic film into the electrolyte (anodic material). At the same time the electrons are injected into the electrochromic film from the transparent conductor (cathodic material), or extracted from the electrochromic film into the transparent conductor (anodic material). The electrons are needed to preserve charge neutrality. Reversing the voltage polarity brings back the original properties [6].

The electrochromic material is optically active material in the electrochromic device. It is deposited in a form of

thin film on the top of the transparent conductor. Electrochromism is known to exist in many types of materials, both organic and inorganic. Among the inorganic, the most attractive are transition metal oxide and transition metal hexacyanoferrates.

Iron(III) hexacyanoferrat(II), also known as Prussian Blue (PB) is polyelectrochromic material that exhibit four colors. In a form of thin film it has a blue color in as - deposited state, and can be:

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

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

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

$$\underset{\text{PB}}{\left[Fe^{III}Fe^{II}(CN)_6\right]^-} \rightarrow \underset{\text{PX}}{\left[Fe^{III}Fe^{III}(CN)_6\right]^0} + e^- \qquad (2)$$

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

$$\underset{\text{PB}}{\left[Fe^{III}Fe^{II}(CN)_6\right]^-} + e^- \rightarrow \underset{\text{PW}}{\left[Fe^{II}Fe^{II}(CN)_6\right]^{2-}} \qquad (3)$$

2. Materials and methods

Prussian blue [PB, iron(III) hexacyanoferrate(II)] electrochromic thin films have been deposited onto fluorine doped tin oxide (FTO) coated glass substrates commercially available. The films were prepared by chemical bath 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, 0.5 g EDTA (Ethylenediaminetetraacetic acid) and 10 ml 3 mol/dm^3 HCl, while the second solution was an aqueous solution of 15 ml 0.1 mol/dm^3 K4[$Fe(CN)_6$], 90 ml H_2O and 10 ml 3 mol/dm^3 HCl. 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 [9]. The thickness of the films depends on the number of immersion cycles. In this work PB films were deposited by 20 cycles, which results with 140 nm thick films.

For practical electrochromic investigations, an electrochromic device was constructed. It consisted of a home built glass cuvette with a 1mol/dm3 KCl (slightly acidified with 2 drops of conc. HCl in 100 ml of the solution) aqueous 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). Figure 1 depicts the cross section of the so – designed ECTD.

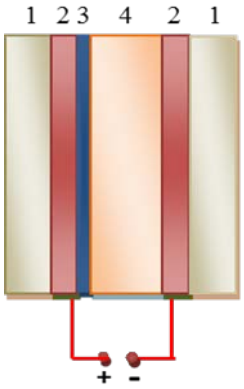

Figure 1: Cross-section of the ECTD: 1 - glass, 2 - FTO, 3 - PB film, 4 - electrolyte

In order to determine optical properties of the obtained films spectro-electrochemical techniques were used. The visible transmittance spectra were recorded in-situ using Varian CARY 50 Scan UV-Visible spectrophotometer, in the wavelength range from 350 to 900 nm in both, the completely bleached and colored states of the films. The bleaching and the coloring of the films were performed with applied voltages of -2 V, -1V, and +2 V. A transparent glass cuvette with two clean FTO coated glass substrates, filled with electrolyte, was measured as 100 % background. The measurement of the relative transparency spectra was done by accuracy of 0.001 or 0.1%, while the accuracy of the light wavelength was 0.1 nm.

From the transmittance data (T), and the film thickness (t), the absorption coefficients spectra, in the bleached and colored states of the films, were calculated using the equation:

$$\alpha(\lambda) = \frac{1}{t} \ln \frac{1}{T(\lambda)} \qquad (4)$$

The spectral intensity of the transmitted (modulated) solar irradiance through the films was calculated by the equation:

$$I(\lambda) = I_0(\lambda) e^{-\alpha(\lambda)t} \qquad (5)$$

where $I_0(\lambda)$ is the spectral intensity of the incident irradiation. The AM 1.5 solar irradiance spectrum [10] was used as reference. The calculated output spectral intensities within the visible region, transmitted across the PB thin films in their bleached, blue and green states, were numerically integrated. The relative change of the integrated intensity (the visible transmitted intensity and the light modulation) can be calculated [11] by the equation:

$$M = \frac{I_{tb} - I_{tc}}{I_{tb}} \qquad (6)$$

where I_{tb} and I_{tc} are integrated transmitted intensities of the films in ther bleached and colored states respectively, and M is the integrated intensity modulation of the solar illumination.

3. Results and discussions

PB films investigated in this work exhibited good electrochromic properties. The films had deep blue color in as deposited state, and changed 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) transparent (-2V), B) blue (-1V) and C) green (+2V).

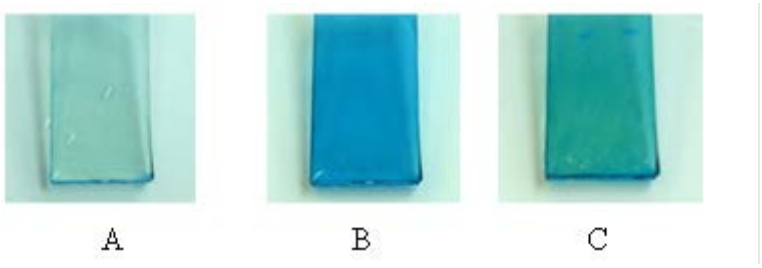

Figure 2: Photographs of chemically deposited PB thin films in: A) transparent, B) blue and C) green states.

The transmission spectra of the PB film, in the wavelength range from 350 to 900 nm, in: transparent, blue, and green states, are presented in Fig. 3. As can be seen, the film has different spectral transmission in different states.

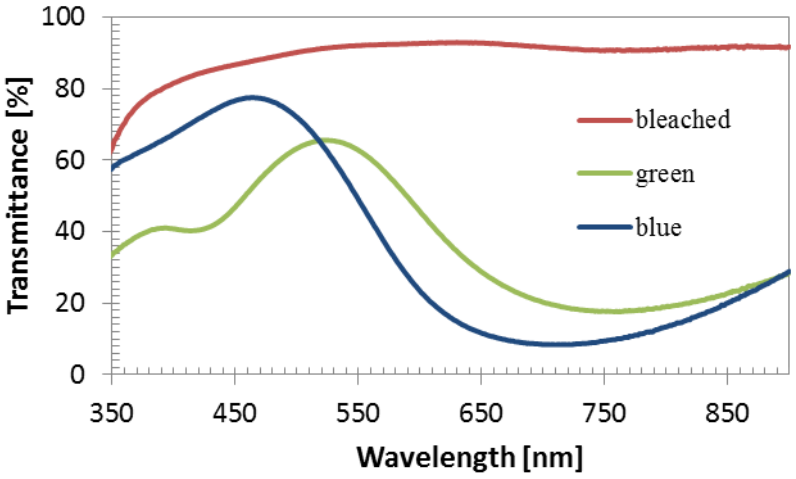

Figure 3: In-situ visible transmittance spectra of chemically deposited PB thin film in transparent, green, and blue states.

Figure 4 shows absorption coefficient spectra calculated from the equation (1) for the PB film in its transparent, blue, and green states. These spectra were taken as input parameters together with the AM 1.5 irradiance solar spectrum. The output intensities transmitted across the PB film, in the transparent and blue states, as well as in

the transparent and green states were calculated by the equation (2) and presented in Fig. 5 and 6.

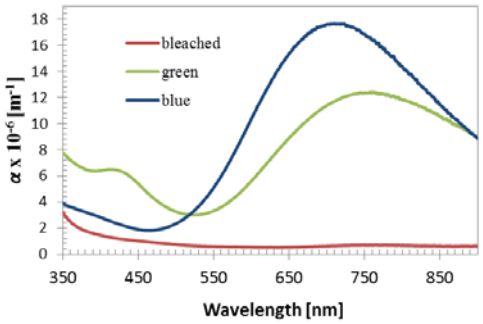

Figure 4: Absorption coefficient spectra of chemically deposited PB thin film in transparent, green, and blue states.

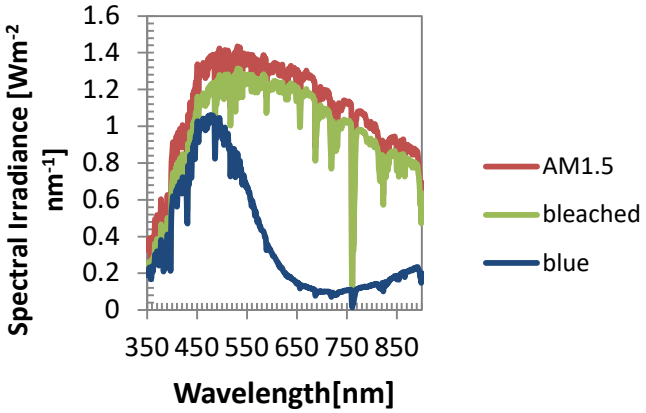

Figure 5: Spectral intensity of the transmitted AM 1.5 solar irradiance spectrum through the PB film in its transparent and blue states.

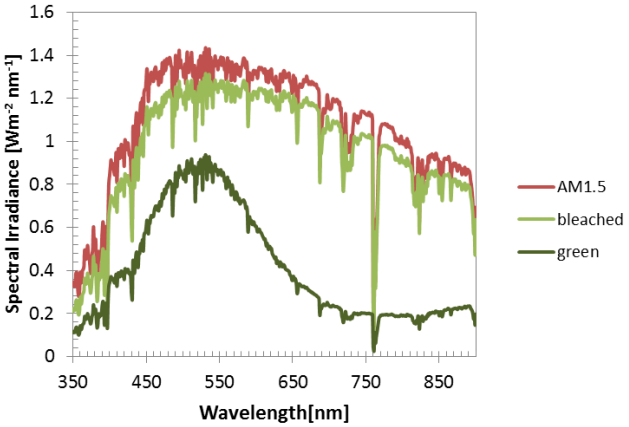

Figure 6: Spectral intensity of the transmitted AM 1.5 solar irradiance spectrum through the PB film in its transparent and green states

The results of the numerical integration for the spectral intensity within the visible region (350 – 900 nm), and the integrated intensity modulation of the solar illumination M in the same wavelength region are presented in the Table 1.

Table 1: Integral transmitted intensity from 350 to 900 nm through the PB films in their bleached and colored states.

States	I_{tb} (W/m^2)	I_{tc} (W/m^2)	M (%)
Transparent - blue	531,43	210,06	61%
Transparent - green	531,43	224,51	58%

As can be seen from the Table 1, the integrated intensity modulation of the solar illumination of about 61 % was obtained by switching the film between transparent and blue states, and 58% by switching it between transparent and green states, which gives opportunity for implementation of chemically deposited PB films in electrochromic devices such as the “smart windows”.

4. Conclusions

Prussian Blue thin films were deposited onto FTO substrates by chemical bath deposition method. Obtained films revealed electrochromism changing color from blue to green at +2 V, from green to blue at -1 V, and became transparent at -2 V. The maximum light intensity modulation ability of the films, as the AM 1.5 spectrum is taken for an input, was calculated to be about 61% by switching the film between transparent and blue states, while the maximum light intensity modulation abilities by switching the film between transparent and green states was calculated to be about 58%. These considerable values make PB thin films suitable for application in electrochromic devices.

5. Recommendations

The article mentioned on energy efficiency with electrochromic Prussian Blue thin films was conducted at laboratory scale with liquid electrolyte. So, in order to apply for practical applications, further studies with solid electrolyte should be done. Also, the weather capabilities of the all-solid state system should be tested.

References

[1] Velevska J., Pecovska – Gjorgjevich M. and Stojanov N., “Electrochromic nickel oxide thin films for solar light modulation”, International Journal for Sciences: Basic and Applied Research (IJSBAR), vol 31(3), pp 94-104, 2017

[2] Dussault J. M., Gosselin L. and Galtsian T., “Assesment of buildings energy efficiency with smart window glazing curtain walls”, Proceedings of Smart materials, structures & NDT in aerospace

conference, Canada, 2011

[3] Casini M., "Smart windows for energy efficiency of buildings", Proceedings of Second International Conference on Advances in Civil, Structural and Environmental Engineering – ACSEE, pp 273-281,

[4] Syrrakou E., Papaefthimou S., Skarpentzos N. and Yianoulis P., "Electrochromoc windows: physical characteristics and environmental profile", Ionics, vol 11, pp 281-288, 2005

[5] Sanders H., Podbelski L., "Electronically tintable glass: The future of high perfomance facades is here", Proceedings of Buildings Enclosure Science & Technology (BEST2) Conference, pp 1-14, 2010

[6] Arman S., "Electrochromic materials for display application", J. New. Mat. Electrochem. Systems, vol. 4 pp 173-179, 2001

[7] Mortimer R. J. and Rosseinsky D. R., "Electrochemical polyelectrochromicity in iron hexacianoferrate films, and a new film form of ferric ferricyanide" J. Electroanal. Chem., vol. 151, pp 133-147, 1983

[8] Mortimer R. J. and Rosseinsky D. R., "Electron-transfer processes and electrodeposition involving the iron hexacyanoferrates studied voltammetrically", J. Chem. Soc. Dalton Trans., vol 5, pp 991-994, 1983

[9] Demiri S., Najdoski M. and Velevska J. „A simple chemical method for deposition of electrochromic Prussian blue thin films", Mater. Res. Bull. vol. 46, pp 2484-2488, 2011

[10] ASTM GI73-03 Standard Tables for Reference Solar Irradiances: Direct Normal and Hemispherical on 37^0 Tilted Surface (2012)

[11] Ristova M., Neskovska R. and Mircevski V., "Chemically deposited electrochromic cuprous oxide films for solar light modulation", Sol Energy Mater Sol Cells, vol 91, pp 1361-1365, 2007