



Electrochromic Characterisation of Electrochemically Prepared Prussian Blue Thin Films

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IN THIS paper, Prussian Blue (PB) thin films were deposited on indium Tin Oxide (ITO) transparent electrode using electro-deposition technique. The films are easily prepared by successive immersion of the substrates into an aqueous solution of FeCl_3 and $\text{K}_4[\text{Fe}(\text{CN})_6]$. The effect of the molar concentration during deposition process of the films is studied. The prepared films were subjected to electrochemical ion insertion using electrochemical cell containing 1M KCl aqueous solution. The electrochromic properties of samples prepared at different conditions were studied by transmittance and reflectance measurements. Also, structure of and morphology for the as-deposited sample prepared at solution molarity of 0.04 M are studied using (XRD) and scanning electron microscopy (SEM).

Keywords: Electrochromic; Prussian blue; Optical properties; Solution concentration; X-ray.

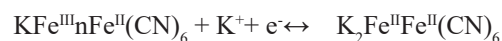
Introduction

Electrochromic, a reversible change in a material's optical properties (transmittance, absorption and reflectance) under an applied voltage [1], is an old phenomenon which was discovered 40 years ago [2]. Since its discovery, considerable progress has been achieved in the syntheses of electrochromic (EC) materials, the fabrications of EC devices, the improvements of EC properties and the applications of EC materials that have been extended to smart windows, displays, antiglare mirrors and active camouflages[3].

Many organic and inorganic materials exhibit EC properties. Common viologens [4], polyaniline (PANI) [5], poly(3,4-ethylenedioxythiophene) (PEDOTs) [6] are common organic and polymer EC materials; while inorganic EC materials include WO_3 [7], NiO [8, 9], TiO_2 [10], V_2O_5 [11] and PB [12].

Electrochromic properties of Prussian blue (PB) materials were observed by Neff[13] only

in 1978. The first use of this blue coloured material was for dyeing the uniforms of Prussian soldiers, thus was named Prussian blue. After that, it was used as carbon paper dye and also in paints and pigments [14]. Prussian blue (PB), $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ belongs to a transition metal hexacyanometallate family[15] and is the oldest coordination compound known and used[16]. Prussian blue (PB), ferric(III) hexacyanoferrate(II), has attracted widespread interest in electrochemistry during recent years[17]. Prussian blue has been described in two formulations, the "soluble" form, $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$, and the "insoluble" form, $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot 6\text{H}_2\text{O}$. PB films show electrochromic behaviour associated to their redox state. The reaction that describes the reduction of "soluble" PB to ES is given by:



(blue)(Colourless)

PB thin films are generally prepared by electrochemical deposition methods, immersion

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of the substrate in a hot solution [18], pulsed electrodeposition [19], and sacrificial anode (SA) method [20]. PB has been studied by voltammetry [21] and galvanometry.

Nowadays, its application range covers very different in research areas such as clinical diagnostic or treatment [22], conducting polymers [23], electrochromic displays [24], fuel cells [25], batteries [26], sensors and biosensors [27] or electrocatalysis [28]. Besides this, a noticeable interest in magnetic properties of Prussian blue type systems has been observed in the last few years [29]. The benefits of an intensely coloured inexpensive blue pigment, flexible in its handling properties and not gritty or difficult to use, were obvious.

This work aims to study the effect of solution concentration as a preparation parameter on the electrochromic properties of PB films by transmittance and reflectance measurements. Also, the film structure as well as surface morphology of the prepared films are also studied.

Experimental work

Potassium ferrocyanide ($K_4[Fe(CN)_6]$, >99%) soluble in water Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, >97%) soluble in water, Potassium chloride (KCl > 99%), Hydrochloric acid HCl (ACS reagent, 37%) and distilled water. Indium-tin oxide (ITO) transparent conductor substrate with a sheet resistance of $15\Omega/\square$, was used as a cathode while the anode was a platinum sheet of (0.5x 2.5)cm. A dc voltage of 0.5 Volt was applied during deposition process. The current was kept constant during the deposition. All the prepared samples were deposited at room temperature.

The solution for electrodeposition is simply prepared by mixing 10ml of (0.05 M, $K_4[Fe(CN)_6]$) with 10 ml of (0.05M, $FeCl_3 \cdot 6H_2O$) and 5 ml of (0.05M, HCl) in 50 ml beaker. For complete dissolving the solution was turn it with a glass leg for 5 min at room temperature. We were considerate addition HCl, then $K_4[Fe(CN)_6]$, and then $FeCl_3 \cdot 6H_2O$. The mixed solution should be prepared just before use. Dip the electrodes in to the solution prepared above for 2 min, the distance between the two electrodes were about 1.5 cm. The electrodes were rinsed in a distilled water and then return it to the solution and repeat this step until we reached to the desired precipitation time.

In this work, thin films of Prussian blue have been prepared with different concentrations

at a constant deposition time (20 min.) . Classification of samples with concentration is shown in Table 1.

TABLE 1. Classification of samples with solution concentration during deposition process

Sample	Solution concentration (M)
M1	0.04
M2	0.05
M3	0.06
M4	0.08
M5	0.1

The spectral absorbance is calculated from the following relation

$$R(\lambda) + T(\lambda) + A(\lambda) = 1 \quad (1)$$

The visible, T_v , transmittance of the prepared samples were obtained by integrating the measured transmittance, $T(\lambda)$, weighted by the solar spectrum at air mass 2 (AM2) [30] and can be given as

$$T_v = \frac{\int_{380}^{780} T(\lambda) G(\lambda) d\lambda}{\int_{380}^{780} G(\lambda) d\lambda} \quad (2)$$

where $G(\lambda)$ is the solar intensity curve.

The change in the visible optical density is a term used to compare the electrochromic properties of the films [29] and can be defined as

$$\Delta(OD) = \log(T_{vb}) / (T_{vc}) \quad (3)$$

where T_{vb} , T_{vc} are the calculated visible transmittance in the bleached and coloured states, respectively.

In order to characterise the electrochromic properties, the prepared samples were subjected to electrochemical ion insertion (colouring state) / extraction (bleaching state) in an electrochemical cell containing KCl aqueous solution. The potential used for colouring and bleaching of the prepared films was $\pm 1.5V$. The spectral transmittance, $T(\lambda)$, was recorded using double beam spectrophotometer model (JASCO-V-670) in the wavelength range from 350-850 nm. The structure of the prepared films was investigated at ambient temperature using x-ray technique using PW 1710 control unit Philips, its anode material was Cu, and it was used at 40 K.V. The morphology of films measured by a scanning

electron microscopy, SEM, (JEOL JEM 1230, Japan) model.

Results and Discussion

Optical properties

The optical transmittance and reflectance of the prepared films were studied in the wavelength range 350-850 nm. A potential of +1.5 V was used for insertion of ions (colouring state) and -1.5 V for extraction of ions (bleaching state). Figs (1-5) show the transmittance and reflectance in bleached and coloured states for samples prepared at different concentration (0.04, 0.05, 0.06, 0.08 and 0.1), respectively. It is clear that the spectral transmittance for samples prepared

at solution concentrations of 0.04, 0.05 Mol. Possesses a quite high values of transmittance in the bleached state and the values of the spectral transmittance at 550 nm are (63.3%, 62.9%) respectively. However, samples prepared at higher solution concentrations (0.08 and 0.1) have quite low values of transmittance, $T(\lambda)$ at 550 nm are 34.4 and 28.7%, respectively. These results are analogous to that obtained by Elshorbagy et al.[31]. In contrast, the transmittance values after colouration for all samples are quite low. Also, There is no appreciable change in spectral reflectance with wavelength in both bleached and coloured states and it has an average values less than 10% for all of the samples.

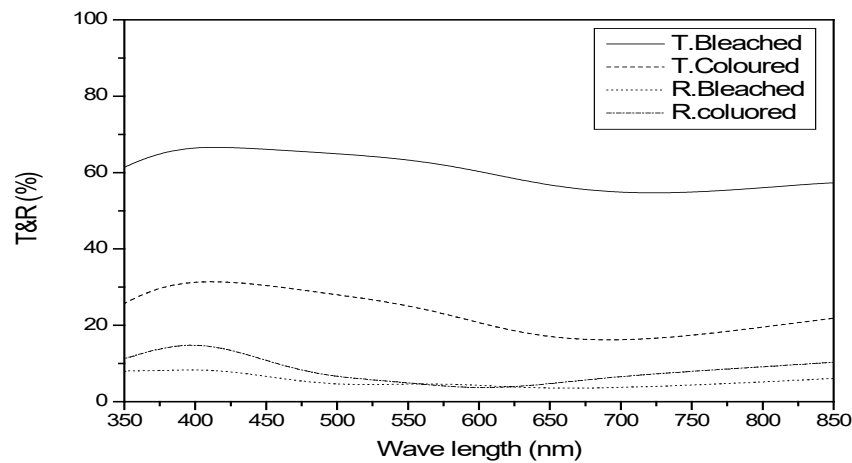


Fig.1. The transmittance and reflectance as a function of wavelength in both bleached and coloured states for sample (M1) prepared at a solution concentration of 0.04 mol .

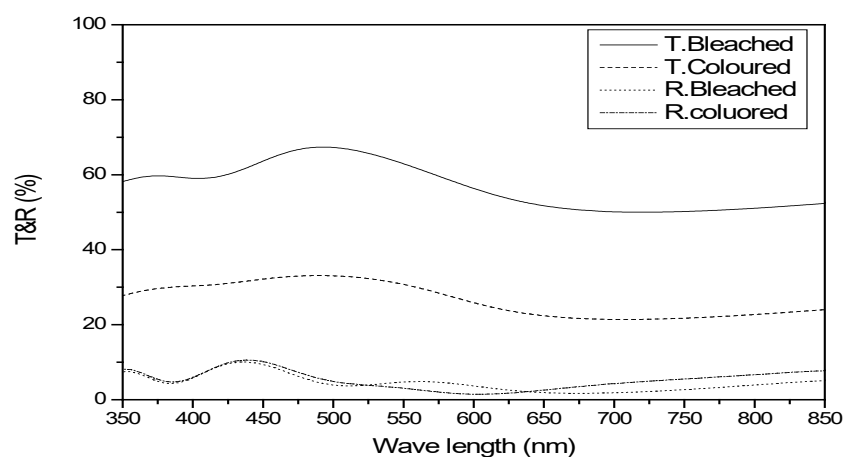


Fig.2. The transmittance and reflectance as a function of wavelength in both bleached and coloured states for sample (M2) prepared at a solution concentration of 0.05 mol.

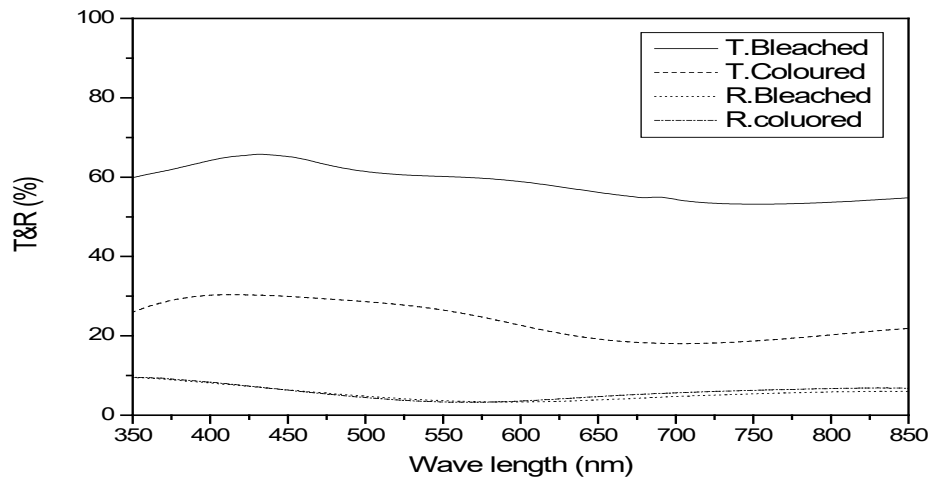


Fig. 3. The transmittance and reflectance as a function of wavelength in both bleached and coloured states for sample (M3) prepared at a solution concentration of 0.06 mol.

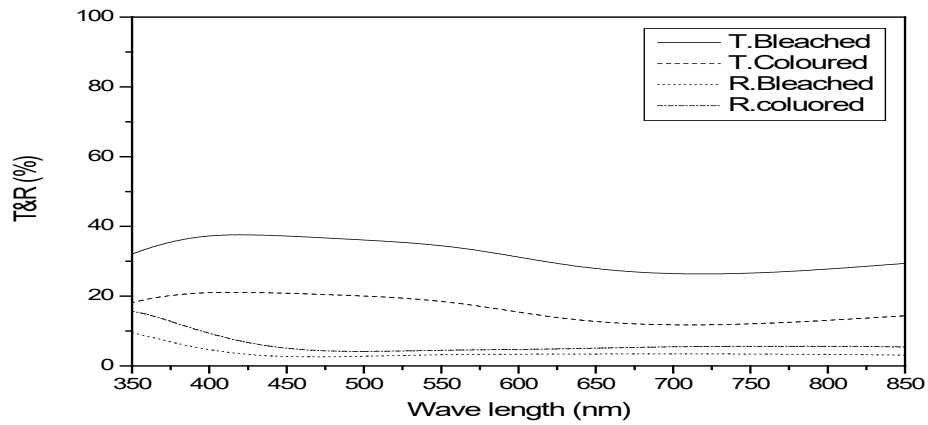


Fig. 4. The transmittance and reflectance as a function of wavelength in both bleached and coloured states for the sample (M4) prepared at a solution concentration of 0.08 mol.

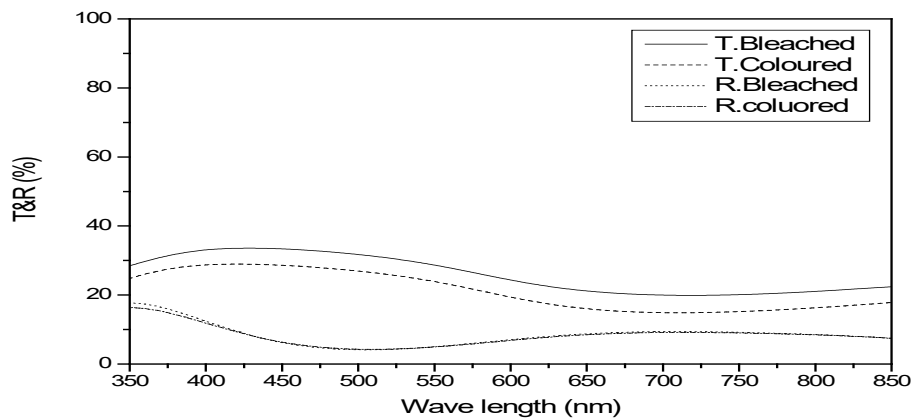


Fig. 5. The transmittance and reflectance as a function of wavelength in both bleached and coloured states for the sample (M5) prepared at a solution concentration of 0.1 mol.

Figure 6 show the spectral absorption as a function of wavelength in both bleached and coloured states for the sample (M1) prepared at a concentration of 0.04 mol . It is clear that the sample in the coloured state possesses quite high values of absorption. For example at a wavelength of 550 nm, the values of absorption are 0.32, 0.70 in the bleached and coloured states, respectively. This means that PB films can be classified as “absorption modulated films”.

The dependence of the transmittance change ΔT_v [$\Delta T_v = (T_{v, \text{bleached}} - T_{v, \text{coloured}})$] on the solution concentration during deposition of the films is shown in Fig .(7). It is obvious that samples prepared at concentrations of 0.04 and 0.05 exhibit a very good electrochromic behaviour, where the difference in ΔT_v is (~ 0.32) in both cases. Comparing with samples prepared at concentrations of 0.08 and 0.1 $\Delta T_v = 0.18$ and 0.05, respectively.

Also the change in the visible optical density with concentration is depicted in Fig. (8). It is clear from the figure that samples prepared at concentrations of 0.04 and 0.05 mol. possesses higher values of optical density (0.28). Films prepared at higher concentrations possesses a lower values of optical density (e. g. for a sample prepared a concentration of 0.08 mol has an optical density of 0.23).

Structure properties

The structure properties of the as deposited films prepared at 0.04 mol were defined by x-ray diffraction. Fig. (9) shows the XRD pattern of the as deposited PB sample (M1), deposited on ITO substrate. It is clear that the sample is in the amorphous state. The diffraction peaks in the pattern is correspond to $\text{In}_2\text{Sn}_2\text{O}_7$ back substrate. This result is in convenient with Demiri et al.[32].

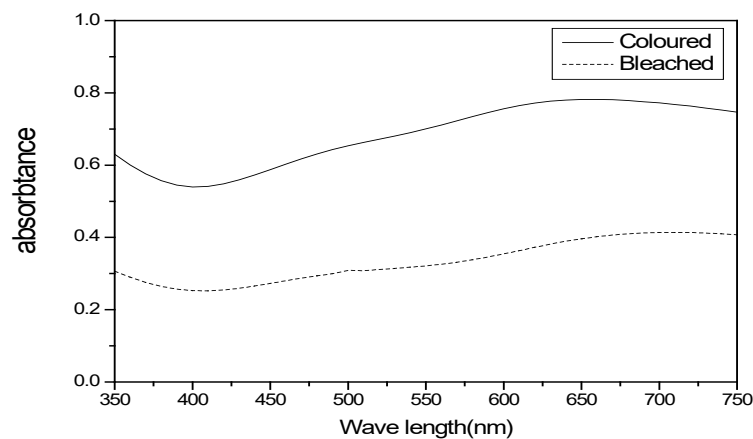


Fig. 6. The spectral absorption as a function of wavelength in both bleached and coloured states for the sample (M1).

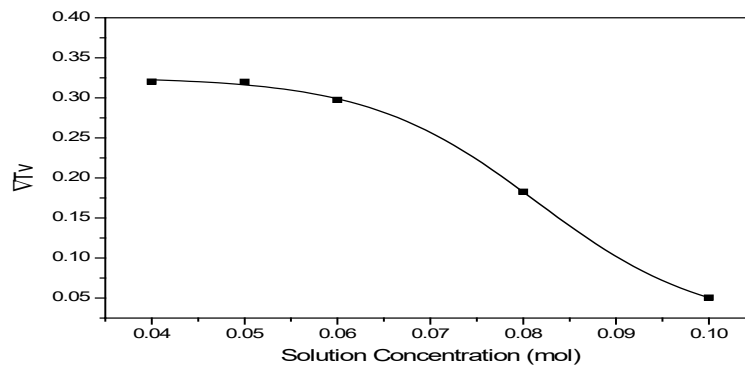


Fig.7. The transmittance change (ΔT_v) as a function of the solution concentration.

The morphology properties

SEM was used to illustrate the surface structure and morphology of the as deposited sample (M1) which possesses good electrochromic properties and is shown in Fig. (10).

It can be observed that the film has a small grain diameter ($\sim 43\text{nm}$) and some large grain. A good electrochromic behavior can be achieved with films which have a small grain size, i.e., large grain boundaries [33].

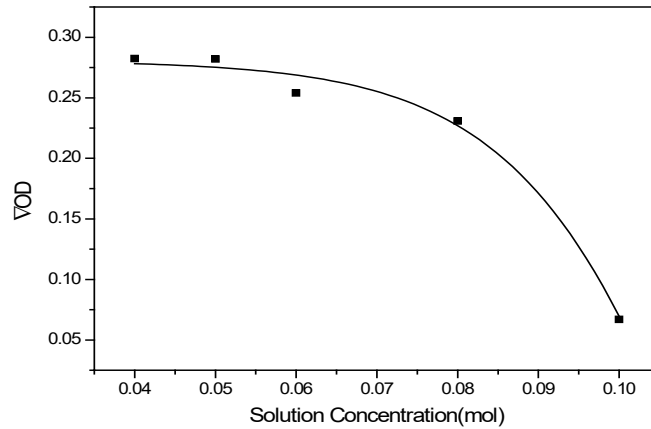


Fig. 8. The change in the visible optical density (ΔOD) with solution concentration.

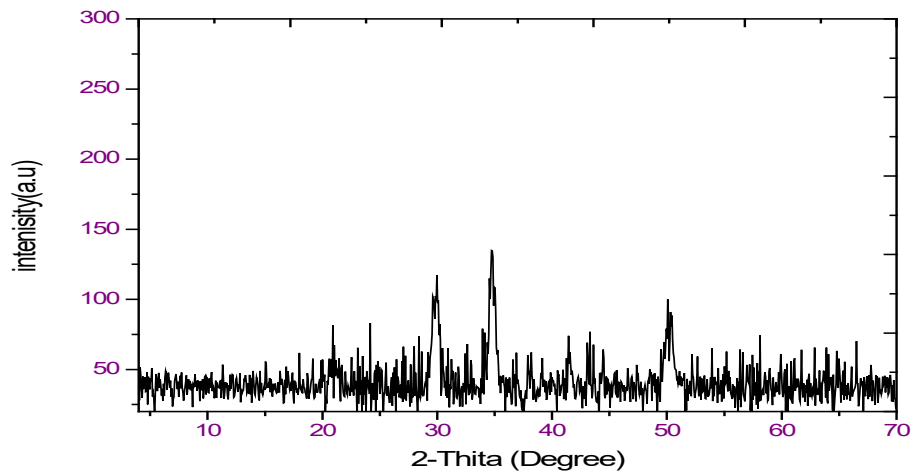


Fig. 9. X-ray diffractogram of PB (M1) film in the as-deposited state deposited on ITO coated glass substrate.

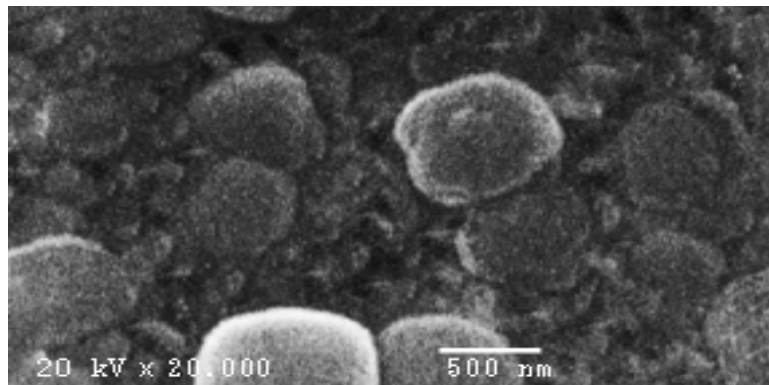


Fig. 10. The surface morphology of the as deposited sample (M1).

Conclusion

Prussian blue thin films were prepared by a simple and economical chemical deposition method. The samples were deposited onto ITO transparent conductor coated glass substrates at room temperature. Colouring and bleaching films were obtained by oxidation and reduction in 1 M KCl electrolyte using a potential of ± 1.5 V. The electrochromic properties of the prepared films were found to be affected by the concentration of solution during deposition process. Films prepared at concentration of 0.04 and 0.0 have a good electrochromic properties ($T_v = 0.32$ and $OD = 0.28$). However, films prepared at higher solution concentrations possess a low dynamic range (e.g. sample (M5) has $T_v = 0.05$ and $OD = 0.07$). X-ray diffraction shows that the films of amorphous for 0.04 (M1) concentration Prussian blue. SEM analysis shows that the sample (M1) which possesses a good electrochromic properties has a small grain diameter (~ 43 nm).

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التوصيف الكهرولوني لشرائح رقيقة من مادة الازرق البروسي المحضرة كهروكيميائيا

أسماء حفناوى، كمال عبدالهادى و صفوت أحمد على
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في هذا البحث تم تحضير افلام ازرق بروسى (PB) بواسطة طريقة ترسيب كيميائية بسيطة واقتصادية فى درجة حرارة الغرفة، على شرائح زجاجية سبق طلاؤها بموصل شفاف ITO عند تركيزات مختلفة للمحلول المستخدم، تم الحصول على التلوين والتبييض للافلام عن طريق الاكسدة والاختزال فى محلول الكتروليتى من كلوريد البوتاسيوم KCl بتركيز 1M عند فرق جهد يساوى ± 1.5 فولت. وقد وجد ان الخصائص الكهرولونية للافلام المترسبة تتأثر بتركيز المحلول المستخدم اثناء عملية الترسيب. حيث ان الافلام التى تم تحضيرها عند التركيزات 0.04 و 0.05 مول تمتلك خصائص كهرولونية جيدة حيث وجد ان متوسط الفرق فى النفاذية فى المدى المرئى للافلام المحضرة فى حالتى التلوين (T_{vc}) والتبييض (T_{vb}) حيث $\Delta T_v = T_{vb} - T_{vc}$ وكذلك التغير فى الكثافة الضوئية (ΔOD) تساوي ($\Delta T_v = 0.32$ and $\Delta OD = 0.28$). ومن خلال حيود الاشعة السينية تبين ان افلام PB المحضرة عند تركيز 0.04 هى افلام غير متبلورة، وباستخدام جهاز المسح الضوئى للمجهر الالكترونى اظهر ان سلوك الافلام الكهرولونية يعتمد على حجم الحبوب والمسافات البينية الموجودة بينها بالنسبة لتلك الافلام التى تم تحضيرها. ووضح المسح المجهرى الالكترونى لنفس العينة ان فيلم PB ظهر فى حالة متجانسة .