

Digital video electrochemistry (DVEC) applied to the study of Prussian Blue films

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Prussian Blue films were electrogenerated on a Pt disc electrode and color changes were studied by digital video electrochemistry together with cyclic voltammetry. Three systems of peaks were detected. Peaks corresponding to the reduction to the Everitt's Salt form and to the oxidation to Prussian Yellow are well related to color changes expressed as color intensities

derivatives. Color changes showed that these peaks involved complexes mechanisms and intermediate species were detected. These also showed the existence of different sites of iron atoms in the crystal structure with different reactivity. A non-zero baseline and a third electrochemical process at the more negative potentials proved not related to color changes.

Introduction

Prussian Blue (PB, ferric ferrocyanide) is a well-known compound, characterized by its electrochromic properties and good stability if deposited as thin films on different substrate electrodes.^[1–4] However, there is still some controversy about the stoichiometric formula of PB and its electrochromic reactions. The structure has been described as cubic face centered with one quarter of high spin iron vacancies.^[5–7] That makes two different iron sites in this structure, Fe near the vacancies (25 %) and the rest (75 %).^[8–10] Both Fe sites in the PB structure show different electroactivity and electrochromic properties.^[7,11,12]

PB films can be electrogenerated by different procedures, from chemical deposits to electrodeposits (potentiostatic, galvanostatic or voltametric generation) resulting PB films with different electrochemical properties depending on the methodology.^[1,4,13] For example, the quality of galvanostatically generated PB deposits can be controlled by the rate of electrogeneration (i.e. current). High current deposits show a more amorphous macrostructure and electrochemical cyclic voltammetry (CV) peaks proved higher and thinner than for the more crystalline one.^[9,14,15] It was assumed that PB films electrogenerated by the galvanostatic reduction of Fe(III) to Fe(II) in a ferricyanide + Fe(III) salt initially present the 'insoluble' PB structure described as $\text{Fe}_4^{3+}[\text{Fe}^{2+}(\text{CN})_6]_3 \cdot m\text{H}_2\text{O}$. These films can

be reduced to the colorless Everitt's Salt (ES), also known as Prussian White. After a few CV cycl around the $\text{ES} \rightleftharpoons \text{PB}$ system in a potassium salt solution a change takes place, and films were converted into the 'soluble' PB structure. It was proved that this soluble structure is similar to the insoluble one and the main difference is that K^+ cations are inserted in the water crystalline substructure.^[7] Recent studies estimated a 'soluble' PB structure as $\text{Fe}_4^{3+}[\text{Fe}^{2+}(\text{CN})_6]_3 \cdot [\text{K}_h^+ \cdot \text{OH}_h^- \cdot m\text{H}_2\text{O}]^{[7,12,16]}$ where no important differences between successive CV were observed.^[17,18] This process is also known as stabilization of PB films. If this stabilization does not take place, the oxidation of freshly deposited PB films leads to its degradation on the electrode surface. Besides, PB films previously stabilized show taller and thinner voltametric peaks around the $\text{ES} \rightleftharpoons \text{PB}$ system if compared with non-stabilized films.^[18,19]

Whatever the way of generation, PB films can be reduced to the colorless Everitt's Salt (ES) form or oxidized (after stabilization) to the Prussian Yellow (PY) form.^[20] These electrochemical reactions are also accompanied by mass changes due to the electrical charge balance and several charged species have been identified as possible counterions in these processes.^[9,14] The channels of the PB structure proved only 3.2 Å in diameter and only some smaller hydrated cations can enter the PB film.^[4–6,9] However, some larger cations can be exchanged during the redox processes depending on the rate of electrogeneration.^[9,21]

As their name indicates, there is a color change associated to these electrochemical reactions that makes possible to follow it by spectroscopical techniques too.^[3,22] Absorbance changes of the electrode surface can be related with the electrochemical current passed during the faradaic process by the Lambert-Beer law.^[9,11,22] Derivative of absorbance against the applied potential during a CV experiment show peaks like those obtained for the current, but only associated to these processes causing color changes. The correlation between CV and the derivative of absorbance peaks can help to understand the electrochemical kinetics of these reactions.

Recently, a new way of interpretation of spectroscopical results is proposed. Digital video of the electrode surface was recorded during electrochemical experiments, and then

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synchronized with the electrochemical response.^[24–27] One important advantage is the possibility to achieve experimental results during the normal function of the electrode, in non-rigorous darkness conditions such as spectroscopic techniques require or not transparent electrodes. This video was decomposed into individual frames and analyzed based on the red, green and blue (RGB) color system. This is known as digital video electrochemistry (DVEC) and has been used in the analysis of different electrochromic materials. DVEC takes advantage of a fast digital video camera allowing the acquisition of digital images up to the frame rate of the camera. If compared with spectroscopic techniques, DVEC can only measure up to 256 levels of color by each RGB channel for an 8 bit RGB camera, but visible color changes can be monitored simultaneously at any part on the electrode surface. This last characteristic provides the possibility to measure the color dispersion throughout the electrode surface, and the rate of color evolution at different parts on the electrode surface. The homogeneity of color changes on the electrode surface can be monitored by the standard deviation of color intensities on the surface for the three primary colors.^[24,26] It has been also possible to obtain experimentally a good correlation between time derivative color intensities and the number of chromophores.^[28] This can be theoretically justified for thin films, as in this case.^[26] However, it proves difficult obtaining a good correlation between color intensities and absorbance values since color intensities allows obtaining spectroelectrochemical information, but not absorbance values which could be easily related with concentration.^[29]

DVEC shows promising possibilities for the characterization of the electrode surface processes as the quality of Cu layers by electroplating on non-homogeneous electrodes,^[30] the surface characterization of electrochromic materials on resistive materials^[28] or determination of half-life time of electrochemical reactions.^[25,26]

It is also known that PB films can catalyze different electrochemical processes such as the O₂ reduction.^[31] In these cases, it could be possible to discern between electrochromic reactions and other electrochemical processes without color changes associated and then, to estimate the amount of electrocatalytic reaction taking place.^[23]

The aim of this research is to prove that DVEC is a suitable technique for the study of the PB electrochromic system in potassium salt aqueous solution, allowing high resolution enough to discern different electrochemical processes associated to the formation of intermediate species along the ES $\rightleftharpoons$ PB $\rightleftharpoons$ PY system.

Results and Discussion

PB films were electrogenerated by CV in a FeCl₃ and K₃Fe(CN)₆ 0.0025 M solution. Electrodeposition of PB by CV takes place during the cathodic scan at the most negative potentials, around -1.5 V (Figure 1a). The reduction of ferricyanide anions to ferrocyanide ones causes the formation of the insoluble PB that precipitates on the electrode surface. After the 1st cycle, a

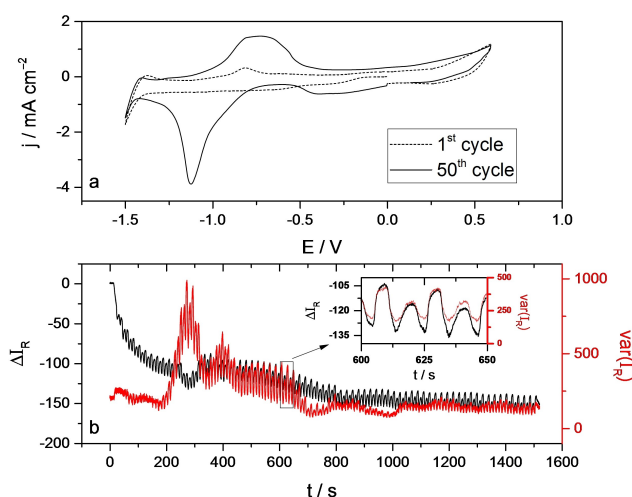


Figure 1. Cyclic voltammetry of PB electrodeposition on a Pt electrode (a) and DVEC data for the red color coordinate during the electrodeposition (b) in 2.5 mM FeCl₃, 2.5 mM K₃Fe(CN)₆ and 0.1 M HCl aqueous solution (pH = 2.0). Scan rate 200 mV s⁻¹.

cathodic voltametric peak at potential -1.15 V appears which increases with the number of cycles. This peak has an associated anodic peak sited around -0.75 V conforming the reversible ES $\rightleftharpoons$ PB system. As the electrodeposition solution is transparent enough, color changes on the electrode surface can be recorded simultaneously to the CV experiment. Figure 1b shows the mean red intensity evolution as representative evolution of other colors. I_R decreases mainly during the first cycles since PB grows on the electrode covering the Pt surface. After 700 s, there is no important color change, since all the surface is covered, and it could be assumed that no more PB is deposited on the electrode. Large values of variance at 300 s are caused by a partial dissolution of the PB formed on the electrode surface (Supporting Information includes a video of the electrodeposition of PB in these conditions). During the last cycles, variance shows no change and minimum values are recorded indicating that the entire surface was covered with Prussian Blue. The small oscillations in color intensity and variance observed during each voltammetric cycle are caused by the electrochemical ES $\rightleftharpoons$ PB $\rightleftharpoons$ PY processes since the electrode changes from blue to transparent and from blue to yellow color (inset in Figure 1b). The height of these oscillations could be a measure of the amount of active PB electro-deposited. During the first scans there is an increase, but during the last cycles no significant change is observed. Then, it could be assumed that no more PB is fixed on the electrode surface.

Before the study of PB films electrogenerated, Pt disc electrode was cycled in a 0.5 M KCl solution with a pH = 2.48 at 20 mV s⁻¹ to reveal any surface electrochemical reaction or any surface color change in these experimental conditions. The sense of potential during the scan was 0.0 V $\rightarrow$ 0.6 V $\rightarrow$ 1.1 V $\rightarrow$ -0.6 V. This experiment was repeated in deaerated solutions by bubbling Ar for 10 min. Figure 2a shows a peak system at potentials about -0.5 V which can be related to the H⁺ adsorption and reduction on

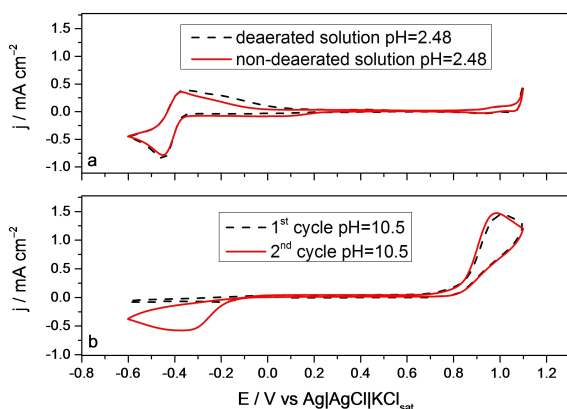


Figure 2. CV of a Pt disc in a 0.5 M KCl solution, pH=2.48 at 20 mV s⁻¹ (a) in deaerated (dashed line) and non-deaerated (solid line) solution, and pH=10.5 at 20 mV s⁻¹ (b) in non-deaerated solution, first cycle (dashed line) and second cycle (solid line).

the Pt surface.^[32] If this experiment is repeated in a pH=10.5 solution, this system of peaks disappears (black line in Figure 2b) which confirms the role of hydronium cations. Between -0.2 V and -0.4 V, there is a cathodic current that can be attributed to the O₂ reduction processes on Pt.^[33] This current proves more evident in the non-deaerated solution of Figure 2a, and also during the second cycle at pH=10.5 (red line in Figure 2b). In this last case, it should be noted that at potentials in the range between 0.8 and 1.1 V there is an important current caused by O₂ evolution, then the solution was saturated in O₂ near the surface electrode causing an important current shoulder at potentials near -0.4 V during this second cycle. No color change during these experiments was observed.

Prussian Blue films deposited on a Pt disc electrode were studied by CV between -0.6 V and 1.1 V in a 0.5 M KCl and pH=3.0 aqueous solution where the fully PB electroactivity is. Figure 3 shows three systems of current peaks located at potentials near -0.45 V, 0.2 V and 0.9 V. Peaks at 0.2 V and 0.9 V were classically associated with the ES ⇌ PB and PB ⇌ PY electrochemical interconversions, respectively.^[4] A cropped video of the electrode surface during the experiment of

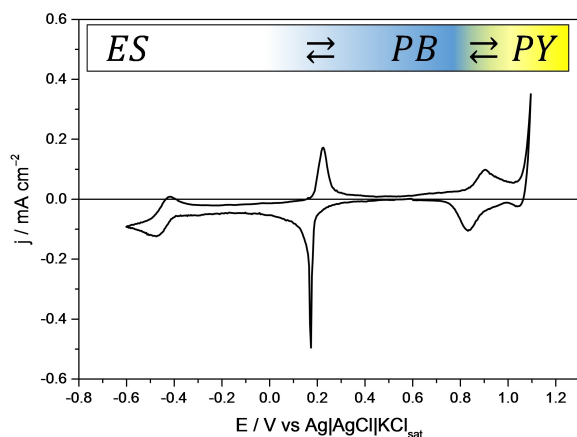


Figure 3. CV of PB in a 0.5 M KCl solution, pH=3.0 at 5 mV s⁻¹

Figure 3 was added to the Supporting Information. In spite that they appear as a single oxidation or reduction peaks, the electrochemical processes involve a more complex kinetic mechanism.^[8,11,20,34]

If one try to analyze these peaks with the classical model for adsorbed electroactive substances, there are some results that could not be explained. Looking at most striking peaks, the peaks near 0.2 V, one can see that the cathodic peak is higher and thinner than the anodic one. On the one side, the half peak width of the cathodic peak reaches only 12 mV and shows a non-symmetrical shape. This half peak width is smaller than that expected for one electrochemical process. On the other side, these peaks show shoulders that can be interpreted as the overlapping of more than one electrochemical process. The participation of H⁺ and K⁺ cations as counterions during the reduction of PB to the ES form have been demonstrated by electrogravimetric studies since there are different electroactive sites on the electrode surface, Fe sites in the crystal structure of PB films described as cubic face centered with 25% of high spin Fe vacancies.^[5-9,34,35] Moreover, a fast analysis of this voltammogram shows that there is a non-zero base line for current caused by the O₂ reduction reaction described in the literature since KCl solutions were not previously deaerated.^[31] Finally, the peaks near -0.4 V are related to the H⁺ adsorption and reduction on the Pt surface. As expected, the reached currents in this process are lower compared with the corresponding peaks in the Figure 2, since PB partially blocks the H⁺ access to the Pt surface. Something similar occurs for the Cl⁻ oxidation around 1 V.

Next, we analyze every electrochemical process within the framework of the color analysis by DVEC. First, let us explain why the mean color time-derivative is better to compare with current of voltammograms. For a given color, the mean intensity (*I*) is proportional to the number of electroactive chromophores in the PB structure (*N_c*):

$$I = k_e (\max(N_c) - N_c) \quad (1)$$

where *k_e* is the proportionality constant here named as apparent electromonochromatic coefficient (mol⁻¹) and it depends on both the analyzed color channel and the electrochromic system analyzed. This constant shows negative values when the oxidized state of the chromophore is darker than the reduced state and, positive values when the opposite occurs. Derivation of Equation (1) is solved as:

$$\frac{dI}{dt} = k_e \frac{d(\max(N_c) - N_c)}{dt} = -k_e \frac{dN_c}{dt} \quad (2)$$

assuming that max(*N_c*) is constant.

Now, we assume that current intensity involves only one electrochromic process (*i_e*) therefore, it depends on the evolution of *N_c* during the electrochemical process (d*N_c*/dt). This can be expressed as:

$$i_c = \frac{dq_c}{dt} = -zF \frac{dN_c}{dt} \quad (3)$$

where q_c is the charge consumed, F is the Faraday's constant and z is the number of electrons per chromophore involved. Then, introducing the Equation (2) into the Equation (3),

$$i_e = -\frac{zF}{k_e} \frac{dl}{dt} \quad (4)$$

we justify the relation between current and the mean color time-derivative which simplifies the RGB color analysis of electrochromic systems.

Going back to our system, Figure 4 shows current and color derivatives changes during the PB $\rightarrow$ ES reduction process. Looking at color changes during this electrochemical process, we observe that the main peak seems to be associated with red color changes. Initially, it seems contradictory that blue color disappears, and the largest color change is obtained for the red channel. However, it is due to the background color of the Pt electrode when the film turns transparent. The initial coordinates for the blue color of PB are high in Blue but low in Red (126,174,191) and after reduction since the ES is transparent, the brilliant Pt surface is observed which Red, Blue and Green coordinates are high enough (203,196,189). Therefore, the color change of PB to ES, significantly increases the red coordinate, but no significant changes in the blue color are recorded.

Looking at dl_B/dt , we observe an initial decrease and after a similar increase. This behavior is characteristic for an intermediate transition between two species. This could be consistent with the electrochemical processes taking place at these potentials where a changeover was found to be determinant in explaining changes in electrical and optical properties of PB.^[11,12,36] This change has been associated to the participation of hydronium cations and can also explain the very narrow voltametric peak which peak potentials agrees with the dl_R/dt peak potential. However, dl_R/dt shows a symmetrical peak

without shoulders, not as the current peak, proving that the Red color peak can be associated mainly to only one electrochemical process. Green color changes are located at slightly more cathodic potentials than the main current peak potentials and the peak appears as a wide peak. Therefore, and according to the DVEC analysis, the cathodic peak should be described as the overlap of at least three different processes. Simulation of CV peaks pointed out to this explanation in the last of 90, and the analysis of EQCM and spectroscopic data confirmed these hypotheses.^[11,34,36,37]

Figure 4 shows color changes bounded between 0.1 V and 0.3 V. Out these limits, we observe that the base line for color changes is zero, that means that the non-zero base line for the current should be attributed to some electrochemical reactions causing faradaic processes which does not involve color changes. As commented before, the reduction of O_2 dissolved in water seems a good explanation for this process. The non-zero baseline has been attributed to the catalysis of the O_2 reduction in the PB structure to form H_2O_2 and finally water.^[31,38]

During the ES $\rightarrow$ PB oxidation process (Figure 5), the electrochemical process takes place by a slightly different mechanism since the peak height and width are different from those of the cathodic one. The dl_R/dt peak appears to be again perfectly synchronized with the current peak, the intermediate species associated with the blue color also appear, but at potentials before the anodic peak. dl_G/dt peak is observed at potentials slightly smaller than the current peak, as in the case of the cathodic one.

A special interpretation deserves the analysis of the peak systems associated with the PB $\rightarrow$ PY oxidation process (Figure 6). Here, the current peak does not show a good coincidence with the Red color change as in the ES $\rightleftharpoons$ PB process. In this case, the 3 color coordinates change along the peak. The first change starts by a decrease in dl_B/dt , together with an increase in dl_R/dt . However, before the dl_R/dt peak, the absolute value of dl_B/dt peak decreases indicating that the blue color does not change at this potential, however, after the

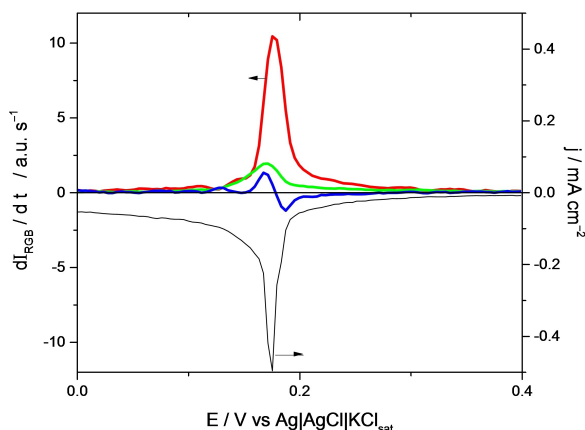


Figure 4. Current and color changes as color intensities derivative (dl_{RGB}/dt) during the CV of the PB to ES reduction process in a 0.5 M KCl solution, pH = 3.0 at 5 mV s⁻¹. Red color corresponds to dl_R/dt , Green color to dl_G/dt and Blue color to dl_B/dt .

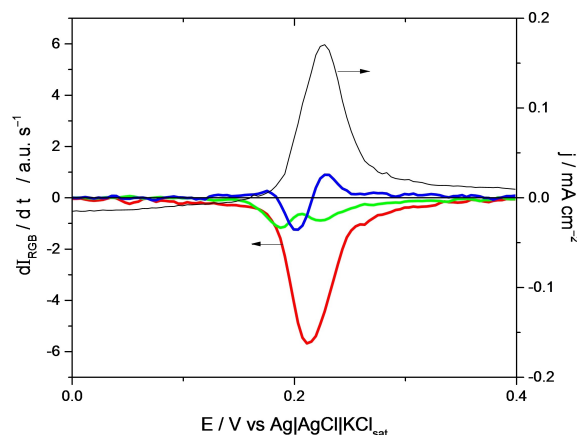


Figure 5. Current and color changes as color intensities derivative (dl_{RGB}/dt) during the CV of the ES to PB oxidation process in a 0.5 M KCl solution, pH = 3.0 at 5 mV s⁻¹. Red color corresponds to dl_R/dt , Green color to dl_G/dt and Blue color to dl_B/dt .

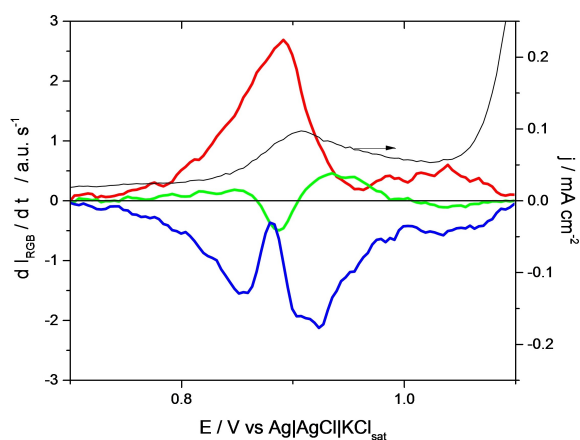


Figure 6. Current and color changes as color intensities derivative (dI_{RGB}/dt) during the CV of the PB to PV oxidation process in a 0.5 M KCl solution, pH = 3.0 at 5 mVs^{-1} . Red color corresponds to dI_R/dt , Green color to dI_G/dt and Blue color to dI_B/dt .

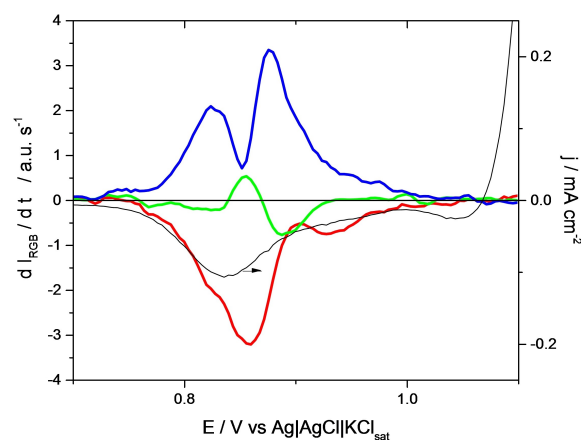


Figure 7. Current and color changes as color intensities derivative (dI_{RGB}/dt) during the CV of the PY to PB reduction process in a 0.5 M KCl solution, pH = 3.0 at 5 mVs^{-1} . Red color corresponds to dI_R/dt , Green color to dI_G/dt and Blue color to dI_B/dt .

maximum of the Red color change, the Blue color changes again, disappearing. The green color shows a double tendency, first a slight increase, then a hard decrease and finally an increase. At potentials where the Green color starts increasing, the intermediate species Berlin Green has been described in the literature.^[20,39,40] At potentials slightly larger than 1.0 V, there is current, a positive Red color change and a negative Blue color change. At these potentials, it has been described that Cl^- anions can enter the PB film acting as counterions balancing the electric charge during the PB oxidation to PY.^[20,41] This reaction takes place after all the K^+ cations have left the PB film. It should be noted also that the electric charge passed during the $\text{PB} \rightleftharpoons \text{PY}$ process proves on the order of 50% of the $\text{ES} \rightleftharpoons \text{PB}$ process since there are less Fe(II) sites than Fe(III) sites in the PB structure and not all Fe(II) sites can be oxidized to Fe(III).^[20,42] Finally, at the more positive potentials current quickly increases, but the three color coordinates keep constant indicating that this electrochemical reaction cannot be attributed to any PB electrochromic processes. As in nude Pt electrode (Figure 2), this current can be associated to the Cl^- oxidation to Cl_2 which does not involve any color change since no mass change has been detected at these potentials.^[20]

The reverse cycle (the PY $\rightarrow$ PB electrochemical process) shows a similar response (Figure 7). At the more positive potentials, high current values but no color change is recorded, then at potentials between 1.0 and 0.9 V blue color increases and the red color decreases, it could mean the reduction of PY to PB by the exit of Cl^- anions, which implies a less yellow color of the films. Then at 0.875 V the blue color shows maximum change, green color disappears, and red color still decreases. Then, Red color coordinates show its maximum change (peak) at 0.85 V and before the current peak. dI_G/dt shows a maximum and Blue color shows a minimum of change. The shape of the dI_G/dt appears to be like an intermediate species change. The Blue color shows its maximum at potentials slightly smaller than the current peak potential, while dI_R/dt shows its maximum at potentials slightly larger than the current peak

potential. That means that Red and Blue color changes are recording information of different processes. The Berlin Green intermediate is also detected associated with the Green coordinate change.

Another interesting point of attention is the system of peaks that appears around -0.4 V (Figure 8), at potentials far from the ordinary electrochemistry of PB. As commented above, the non-zero baseline has been attributed to the catalysis of the O_2 by PB. The first observation is the shape of these voltametric peaks. The system of peaks appears to be reversible for electroactive species in a solution. Comparing with the current response of nude Pt electrode (Figure 2), it could be associated to the formation of adsorbed hydrogen on the Pt surface electrode.

During the cathodic scan, there is no PB color change associated with this electrochemical reaction, however, during the reverse oxidation, an intermediate species seems to be detected by a first PB color decrease, followed by an increase at

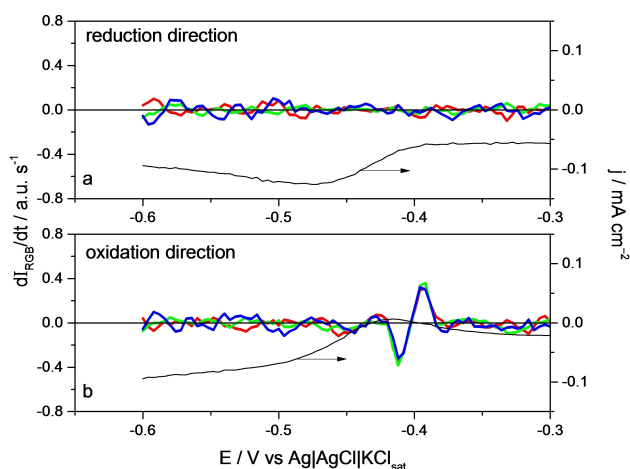


Figure 8. Current and color intensities derivative (dI_{RGB}/dt) during the CV of a PB film between -0.3 V and -0.6 V in a 0.5 M KCl solution, pH = 3.0 at 5 mVs^{-1} . Red color corresponds to dI_R/dt , Green color to dI_G/dt and Blue color to dI_B/dt .

potentials near the anodic peak of current. These color changes may indicate that an intermediate specie reacts with PB, however, this color change has not been observed at largest scan rates voltammograms.

These color changes are not observed during the same experiment without Prussian Blue films on the electrode surface (Figure 2).

Conclusion

Prussian Blue films were studied by digital video electrochemistry (DVEC). Mechanisms for electrochemical processes are not always a single electron reaction. Color changes on the electrode surface were monitored during the electrochemical reactions and more than one process was identified. Color changes during electrodeposition proved larger during the first cycles and after 50 cycles color changes became negligible indicating that all the surface had been covered. During the $\text{ES} \rightleftharpoons \text{PB}$ process, Red color derivatives were well correlated with the main peak current, but Blue and Green color ones seemed to be correlated with the shoulders of the main current peak. The electrochemical process of $\text{PB} \rightleftharpoons \text{PY}$ showed a more complicated mechanism. Berlin Green intermediate was detected at potentials before peak current during the anodic scan. A secondary electrochemical process was detected after the peak current. This process was characterized by color changes and accordingly with the literature with the participation of Cl^- anions as counterions. After, the oxidation of Cl^- to Cl_2 caused a large increase in current but no color change.

The peak at -0.4 V had no significant color change associated indicating that reactions of the media were the main cause. This peak was also observed in nude Pt voltammograms.

Experimental Section

A typical three electrodes cell was used, where the Pt/PB was the working electrode, and a Pt mesh the auxiliary electrode and the $\text{Ag}|\text{AgCl}||\text{KCl}_{\text{sat}}$ was the reference one. All potentials were referred to the later electrode. Pt disc electrodes were cleaned before each experiment first with NH_3 , (Scharlau, 28%), to remove possible PB waste, then with acetone (Scharlau, 99.8%) and finally with HNO_3 (Scharlau, 69.5%). Experimental techniques were controlled by a PAR 273 A potentiostat galvanostat and video was acquired by using a Pontinsic, B01059-P-NT camera up to 30 fps with a resolution of 640×480 pixels. Light was produced by white LED strips (10 W, 6500 K). The cell was an optical glass cell transparent in the Visible.

Prussian Blue was electrogenerated on a Pt disc electrode (0.79 cm^2) by cyclic voltammetry (CV) using the same above mentioned auxiliary and reference electrodes at 200 mVs^{-1} in 2.5 mm FeCl_3 (Scharlau, extrapure), $2.5\text{ mm K}_3\text{Fe}(\text{CN})_6$ (Scharlau, reagent grade) and 0.1 M HCl (Scharlau, 37%) aqueous solution. The potential scan starts at 0.0 V in the negative direction until -1.5 V and after in the positive direction until $+0.6\text{ V}$ during 50 cycles. The electrochemistry of PB was studied by CV in the range of potentials between -0.6 V and 1.1 V in a 0.5 M KCl (Scharlau, reagent grade) aqueous solution ($\text{pH}=3.0$). In KCl alkali solutions ($\text{pH}=10.5$), the pH was achieved by KOH flakes (Scharlau,

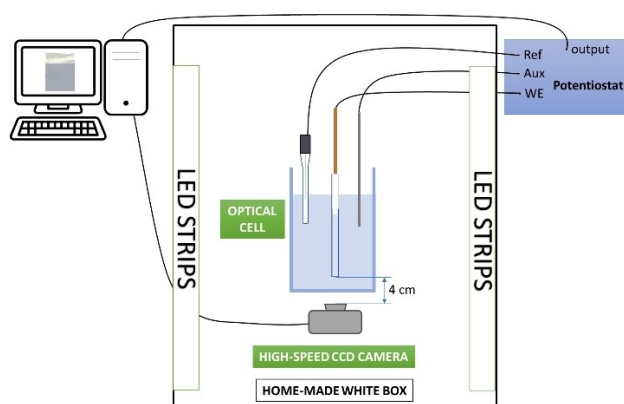


Figure 9. DVEC experimental set-up.

reagent grade). All solutions were freshly prepared with distilled and deionized water (MilliQ-plus, Millipore, resistivity $18.2\text{ M}\Omega\text{ cm}$).

The analysis of DVEC was performed with the help of home-made software. Digital video was first cut, cropped and extracted into individual frames (30 fps), then the selected area was analyzed obtaining the mean color intensity of the color distribution for each RGB coordinate (I_R , I_G and I_B) and the corresponding variance ($\text{var}(I_R)$, $\text{var}(I_G)$, and $\text{var}(I_B)$) by:

$$I_{R, G \text{ or } B} = \left(\sum_{i=1}^{n_{\text{pixel}}} \frac{I_i}{n_{\text{pixel}}} \right)_{R, G \text{ or } B} \quad (5)$$

$$\text{var}(I_{R, G \text{ or } B}) = \left(\sum_{i=1}^{n_{\text{pixel}}} \frac{(I_i - \bar{I})^2}{n_{\text{pixel}} - 1} \right)_{R, G \text{ or } B} \quad (6)$$

where n_{pixel} is the total number of pixels in the cropped image. More details are fully explained previously.^[26,27]

A schema of our experimental set-up is presented in Figure 9. Exposure of the CCD sensor was fixed to avoid artifacts in the color measurement. The experiments were conducted in a closed 'home made' white box which allows keep constant and homogenous the light conditions at any part on the electrode surface. It is important to fix the camera and the electrode positions to facilitate the automatized data analysis.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: conducting polymer · digital video-electrochemistry · DVEC · electrochromic device · prussian blue

- [1] V. D. Neff, *J. Electrochem. Soc.* **1978**, *125*, 886–887.
- [2] D. Ellis, M. Eckhoff, V. D. Neff, *J. Phys. Chem.* **1981**, *85*, 1225–1231.
- [3] R. Mortimer, D. Rosseinsky, A. Glidle, *Sol. Energy Mater. Sol. Cells* **1992**, *25*, 211–223.
- [4] K. Itaya, T. Ataka, S. Toshima, *J. Am. Chem. Soc.* **1982**, *104*, 4767–4772.
- [5] J. F. Keggin, F. D. Miles, *Nature* **1936**, *137*, 577–578.
- [6] H. J. Buser, D. Schwarzenbach, W. Petter, A. Ludi, *Inorg. Chem.* **1977**, *16*, 2704–2710.
- [7] P. R. Bueno, F. F. Ferreira, D. Gimenez-Romero, G. O. Setti, R. C. Faria, C. Gabrielli, H. Perrot, J. J. Garcia-Jareno, F. Vicente, *J. Phys. Chem. C* **2008**, *112*, 13264–13271.
- [8] B. J. Feldman, R. W. Murray, *Anal. Chem.* **1986**, *58*, 2844–2847.
- [9] B. J. Feldman, O. R. Melroy, *J. Electroanal. Chem.* **1987**, *234*, 213–227.
- [10] B. J. Feldman, R. W. Murray, *Inorg. Chem.* **1987**, *26*, 1702–1708.
- [11] J. Agrisuelas, P. R. Bueno, F. F. Ferreira, C. Gabrielli, J. J. Garcia-Jareno, D. Gimenez-Romero, H. Perrot, F. Vicente, *J. Electrochem. Soc.* **2009**, *156*, P74–P80.
- [12] P. R. Bueno, D. Gimenez-Romero, C. Gabrielli, J. J. Garcia-Jareno, H. Perrot, F. Vicente, *J. Am. Chem. Soc.* **2006**, *128*, 17146–17152.
- [13] P. Kulesza, M. Malik, R. Schmidt, A. Smolinska, K. Miecznikowski, S. Zampori, A. Czerwinski, M. Berrettoni, R. Marassi, *J. Electroanal. Chem.* **2000**, *487*, 57–65.
- [14] J. J. García-Jareño, A. Sanmatías, J. Navarro-Laboulais, F. Vicente, *Electrochim. Acta* **1998**, *44*, 395–405.
- [15] J. J. García-Jareño, A. Sanmatías, J. Navarro-Laboulais, D. Benito, F. Vicente, *Electrochim. Acta* **1998**, *43*, 235–243.
- [16] J. Agrisuelas, J. J. García-Jareño, D. Gimenez-Romero, F. Vicente, *J. Electrochem. Soc.* **2009**, *156*, P149.
- [17] R. J. Mortimer, D. R. Rosseinsky, *J. Chem. Soc. Dalton Trans.* **1984**, 2059–2061.
- [18] A. Roig, J. Navarro, J. J. Garcia, F. Vicente, *Electrochim. Acta* **1994**, *39*, 437–442.
- [19] A. Roig, J. Navarro, R. Tamarit, F. Vicente, *J. Electroanal. Chem.* **1993**, *360*, 55–69.
- [20] J. Agrisuelas, J. J. García-Jareño, C. Moreno-Guerrero, A. Roig, F. Vicente, *Electrochim. Acta* **2013**, *113*, 825–833.
- [21] J. J. García-Jareño, A. Sanmatías, F. Vicente, C. Gabrielli, M. Keddari, H. Perrot, *Electrochim. Acta* **2000**, *45*, 3765–3776.
- [22] R. J. Mortimer, *J. Electrochem. Soc.* **1991**, *138*, 633–634.
- [23] J. Agrisuelas, D. Giménez-Romero, J. J. García-Jareño, F. Vicente, *Electrochem. Commun.* **2006**, *8*, 549–553.
- [24] J. Agrisuelas, J. J. García-Jareño, E. Perianes, F. Vicente, *Electrochem. Commun.* **2017**, *78*, 38–42.
- [25] J. Agrisuelas, J. J. García-Jareño, F. Vicente, *Electrochem. Commun.* **2018**, *93*, 86–90.
- [26] J. Agrisuelas, J. J. García-Jareño, E. Guillén, F. Vicente, *J. Phys. Chem. C* **2020**, *124*, 2050–2059.
- [27] E. Guillén, M. Ferrer-Rosello, J. Agrisuelas, J. J. Garcia-Jareno, F. Vicente, *Electrochim. Acta* **2021**, *366*, 137340.
- [28] J. Agrisuelas, J. J. García-Jareño, F. Vicente, *Electrochim. Acta* **2018**, *269*, 350–358.
- [29] Y. Soda, E. Bakker, *ACS Sens.* **2019**, *4*, 3093–3101.
- [30] J. Agrisuelas, J. J. García-Jareño, E. Guillén, F. Vicente, *Electrochim. Acta* **2019**, *305*, 72–80.
- [31] K. Itaya, N. Shoji, I. Uchida, *J. Am. Chem. Soc.* **1984**, *106*, 3423–3429.
- [32] P. S. Lamoureux, A. R. Singh, K. Chan, *ACS Catal.* **2019**, *9*, 6194–6201.
- [33] A. M. Gómez-Marín, R. Rizo, J. M. Feliu, *Catal. Sci. Technol.* **2014**, *4*, 1685–1698.
- [34] J. J. García-Jareño, J. Navarro-Laboulais, F. Vicente, *Electrochim. Acta* **1997**, *42*, 1473–1480.
- [35] P. R. Bueno, D. Giménez-Romero, F. F. Ferreira, G. O. Setti, J. J. Garcia-Jareño, J. Agrisuelas, F. Vicente, *J. Phys. Chem. C* **2009**, *113*, 9916–9920.
- [36] J. Agrisuelas, J. J. García-Jareño, D. Gimenez-Romero, F. Vicente, *J. Phys. Chem. C* **2009**, *113*, 8438–8446.
- [37] C. Gabrielli, J. J. Garcia-Jareno, M. Keddari, H. Perrot, F. Vicente, *J. Phys. Chem. B* **2002**, *106*, 3182–3191.
- [38] H. T. Bui, N. K. Shrestha, K. Cho, C. Bathula, H. Opoku, Y.-Y. Noh, S.-H. Han, *J. Electroanal. Chem.* **2018**, *828*, 80–85.
- [39] Z. Shadike, D.-R. Shi, Tian-Wang, M.-H. Cao, S.-F. Yang, J. Chen, Z.-W. Fu, *J. Mater. Chem. A* **2017**, *5*, 6393–6398.
- [40] R. Mortimer, J. Reynolds, *J. Mater. Chem.* **2005**, *15*, 2226–2233.
- [41] K. Itaya, H. Akahoshi, S. Toshima, *J. Electrochem. Soc.* **1982**, *129*, 1498–1500.
- [42] J. Agrisuelas, J. J. Garcia-Jareno, C. Moreno, F. Vicente, *Electrochim. Acta* **2014**, *138*, 200–209.

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