

Electrochemical Behavior of Electrodeposited Prussian Blue Films on ITO Electrodes

An Attractive Laboratory Experience

J. J. García-Jareño, D. Benito, J. Navarro-Laboulais, and F. Vicente*

Department of Physical Chemistry, University of València, C/ Dr. Moliner 50, 46100 Burjassot, València, Spain

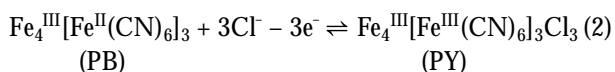
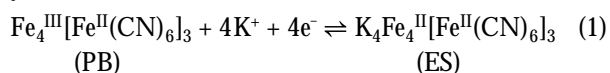
The electrochromic behavior of Prussian blue (PB) deposited onto a transparent electrode is especially attractive to students beginning their laboratory experiences in electrochemistry. The color changes observed during the cyclic voltammetry facilitate the qualitative introduction of such important electrochemical topics as the dependence of composition (ratio of oxidized to reduced state) on the electrode with the applied potential (Nernst equation). The experiment also introduces the student to the measurement of electrochemical magnitudes for the voltammogram. The knowledge of an electrochemical technique as important as cyclic voltammetry is also of interest to students because of its application in several fields, as for example corrosion, electroanalysis, heterogeneous catalysis, characterization of materials, or electrochemical kinetics.

The electrogeneration of Prussian blue, potentiostatically or galvanostatically, makes possible the correlation between the charge transferred during the electrogeneration and the amount deposited on the electrode (Faraday's law). This laboratory experience is aimed at showing the electrochromism and analyzing the voltammogram obtained for Prussian blue electrogenerated films on transparent ITO (indium-tin oxide) electrodes.

Theory

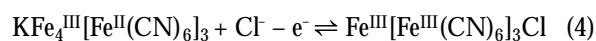
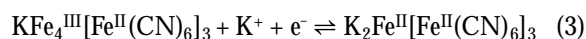
Since Prussian blue was deposited for the first time on a solid electrode by V. D. Neff (1), the interest in this compound has been increasing (2).

Prussian blue (ferric ferrocyanide) presents changes of color associated with the oxidation and reduction processes; that is to say, it is an electrochromic material. Thus, when it is reduced in aqueous medium in the presence of potassium ions the film becomes colorless and is then called Everitt salt (ES). If the oxidation is conducted in chloride medium, a yellow compound known as Prussian yellow (PY) is obtained. The reactions that describe these processes were studied by Itaya et al. (3):



Although at first PB films are deposited as their insoluble form, a structural change is produced in the material when the films are cycled several times in aqueous solutions with potassium ions. This way the film loses about one fourth of the Fe^{III} present in the structure, this amount of Fe^{III} being

replaced by potassium to maintain the film electroneutrality. This latter structure of Prussian blue is known as "soluble" Prussian blue (although it is not soluble). This change can be monitored by a change of the voltammetric peaks, which become higher and narrower (4, 5). But the electrochromic properties of the films are maintained, and the same color changes are seen when PB films are reduced and reoxidized. Studies on the stability of this material have proved that films increase their stability if they are first cycled around the system $\text{PB} \rightleftharpoons \text{ES}$ (the reduction system) several times (6); that is, if they are converted to the "soluble" form. Oxidation and reduction equilibria of the soluble form can be rewritten as follows:



A voltammetric study of PB films at low scan rates, to avoid the contribution of capacitive currents, can be easily done in an electrochemistry laboratory, starting with pretreatment of the electrode surface, continuing with the electrodeposition of films of different thickness and observation of the conversion of the insoluble form into the soluble one, and finishing with the study of the voltammetric waves and their variation with the thickness of the films. The aims of this laboratory experience are:

1. To electrodeposit Prussian blue films onto ITO electrodes;
2. To initiate students into the measurement of electrochemical magnitudes (peak potential, peak current, half-peak potential) from the voltammograms, taking as example the voltammetric waves of PB on ITO and their variation with the thickness; and
3. To observe the electrochromic effect.

Experimental Procedure

ITO Electrode: Pretreatment

The working electrodes were made from a commercial glass/ITO plate (33 × 33 cm) supplied by Glasstone (electrical conductivity of 30 S/m), which was cut into little plates of dimensions 2.5 × 1.0 cm. An electrical contact between the ITO plates and a copper wire was made, secured by means of colloidal silver, and sealed by means of epoxy resin (e. g., Araldit adhesive). Teachers should cut the ITO plates and connect the ITO to the copper wire, because of the time spent making the electrodes and its difficulty for students.

Because the electrodes are reused, a pretreatment is required. The electrode is washed with concentrated ammonia to eliminate all the Prussian blue remaining on it. After this,

it is rinsed with distilled water to eliminate the ammonia. A cleaning with acetone should be done to remove all possible residual organic compounds. Once the electrode has been cleaned with acetone, rinse it again with distilled water.

If an effective surface of about 1 cm^2 is wanted, the upper part of the electrode must be covered with Teflon so that a square about $1 \text{ cm} \times 1 \text{ cm}$ remains bare at the lower part of the electrode (see Fig. 1). The final area of the electrode can be determined by putting a squared paper (in millimeters) below the transparent electrode and measuring the covered area.

Deposits of Prussian Blue on ITO Electrodes

The following solutions should be prepared.

5 mL of a 0.05 M HCl aqueous solution

10 mL of a 0.05 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ aqueous solution

10 mL of a 0.05 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous solution

These three solutions are mixed, in this order, in the electrochemical cell, and the electrodes are immersed in it. An ITO plate, previously treated as indicated, is used as working electrode, Ag/AgCl/ 0.1M KCl is the reference electrode, and a platinum plate is the counterelectrode.

The film is galvanostatically deposited by passing a current of $40 \mu\text{A}/\text{cm}^2$ through the ITO electrode for a given time (t). In this way, 6 electrodes with deposition times of 30, 60, 90, 120, 150 and 180 s should be prepared. Between depositions it is very important to agitate the solution strongly with a glass wire in order to obtain good quality films. Once the film is obtained, it should be rinsed with distilled water and kept away from dust and grease.

It is very important not to immerse the copper wire into the solutions, since secondary redox reactions can take place that damage the electrode.

Voltammetric Curves for Reduction of Prussian Blue on ITO Electrodes in Acidic KCl Solution

Prepare 200 mL of 1 M KCl solution. Add 3 drops of concentrated HCl to the solution, mix, and measure the pH. This provides a medium acidic enough to give a better response of the system.

Every electrode should be treated as follows. First, it should be cycled 15 times between +0.6 V and -0.2 V vs Ag/AgCl/

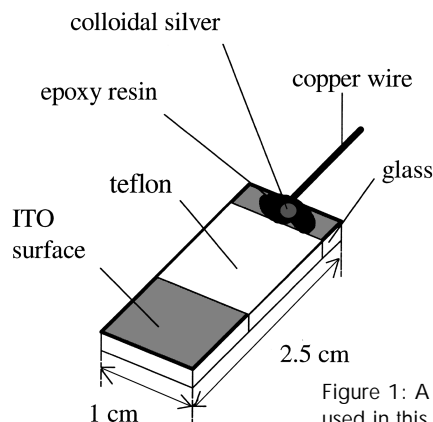


Figure 1: A typical ITO electrode used in this experiment.

1 M KCl (sweep rate 20 mV/s), around the reduction system $\text{PB} \rightleftharpoons \text{ES}$, until the conversion from the insoluble form to the soluble one is produced. Record these 15 cycles and notice the change in the shape of the voltammogram. After this, the electrode is stabilized at +0.6 V for 30 s and a cyclic voltammogram between +0.6 V and -0.2 V is recorded separately in order to study the reduction system. Finally, a complete CV should be recorded. It begins at +0.6 V and goes to -0.2 V to force the reduction of the film; then return to +1.2 V to reoxidize the film, first to the Prussian blue form and then to the Prussian yellow form; finally, return to +0.6 V to reduce the yellow form to the blue one. These experiments should be done in 25 mL of the acidic 1 M KCl solution previously prepared, and using the ITO/PB electrode as working electrode, a Pt plate as counterelectrode, and a Ag/AgCl/ 1 M KCl reference electrode. A scan rate of about 20 mV/s is recommended. It is advisable to write down all the color changes produced during the scan in order to relate them to the voltammetric peaks obtained and to the changes in the oxidation state of the PB films.

All electrochemical experiments were carried out by means of a potentiostat-galvanostat PAR273A. Other potentiostat-galvanostat and recorder equipment, instead of the more expensive PAR273A, can be used without having

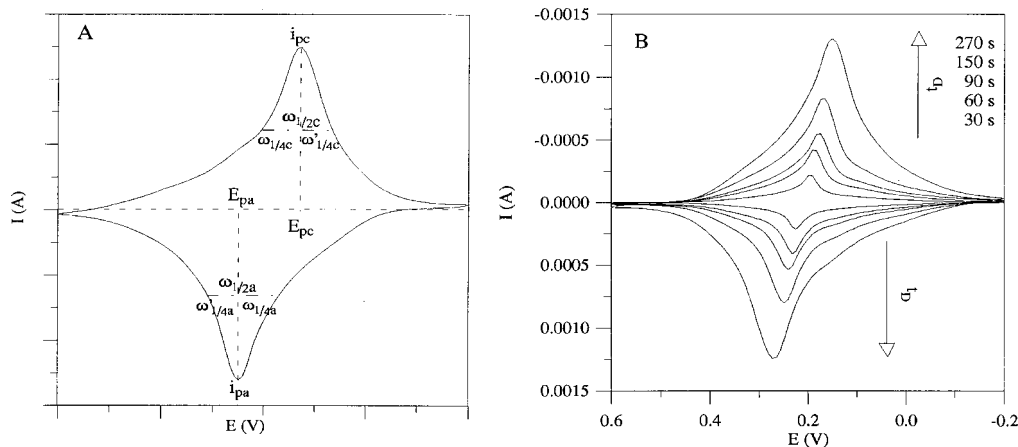


Figure 2: A: Typical cyclic voltammogram of a Prussian blue film on an ITO electrode. The measurement of different magnitudes is shown: E_p , peak potential; i_p , peak current; $\omega_{1/2}$, half-peak width. The c and a subindexes refer to cathodic and anodic peak, respectively. B: CV of PB films on ITO electrode for film thickness after different deposition times t_p . All potentials referred to Ag/AgCl/1 M KCl.

Table 1. Relationship of Experimental Variables to Deposition Time

t_d (s)	Q_c/A (mC/cm ²)	Q_a/A (mC/cm ²)	i_{cp}/A (mA/cm ²)	i_{ap}/A (mA/cm ²)	E_{cp} (V)	E_{ap} (V)	$\omega_{1/2cp}$ (V)	$\omega_{1/2ap}$ (V)
30	-1.22	1.17	-0.20	0.19	0.196	0.227	0.056	0.054
60	-2.56	2.43	-0.34	0.33	0.188	0.232	0.08	0.074
90	-3.83	3.8	-0.48	0.46	0.178	0.241	0.095	0.088
120	-5.23	5.21	-0.64	0.61	0.171	0.248	0.101	0.096
150	-6.79	6.69	-0.78	0.75	0.170	0.249	0.111	0.105
180	-7.95	7.79	-0.89	0.86	0.161	0.258	0.116	0.112

NOTE: Q is voltammogram charge; A is electrode area; i_p is peak current; and E_p is potential peak. The subscripts c and a refer to the cathodic peak and the anodic peak, respectively.

any important effect on carrying out the experiment.

Duration of the Experiment

The time required for the entire experiment, including a brief explanation of the techniques and equipment, pre-treatment of the electrodes, preparation of solutions, deposition of PB, and the voltammetric study, is estimated to be two sessions of three hours.

Results

Measure, for every voltammogram corresponding to the reaction $PB \rightleftharpoons ES$, the value of peak current, peak potential, half-peak width ($\omega_{1/2} = \omega_{1/4} + \omega'_{1/4}$), and voltammogram charge for the anodic and the cathodic peak (Fig. 2). These values are given in Table 1; with these values the formal potential $E^{\circ'}$ can be calculated:

$$E^{\circ'} = \frac{E_{cp} + E_{ap}}{2}$$

It can be seen that the formal potential remains constant, as it should for a reversible process. For a reversible process the Q_c/Q_a and i_{cp}/i_{ap} values must be equal to unity. If those magnitudes are calculated, it can be seen that both of them are close to unity; the deviations from the theoretical value are in the range of the experimental error.

First, the cathodic and anodic peak charge versus the film

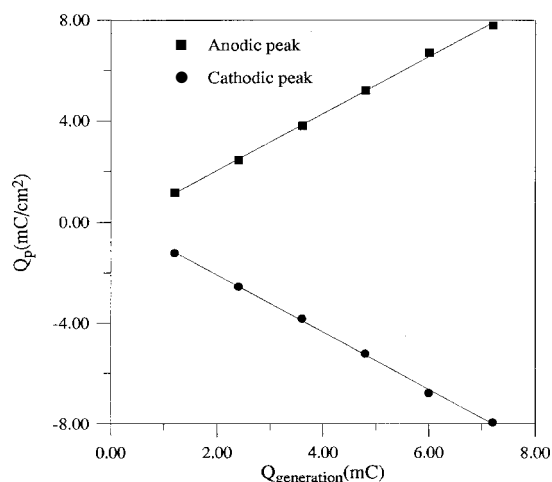


Figure 3. Relationship between the peak charge and the electrogeneration charge for Prussian blue films.

electrogeneration charge Q ($40 \mu\text{A cm}^{-2} \cdot \text{area} \cdot t_d$) is plotted (Fig. 3). Note that this plot fits very well to a straight line. Therefore it is concluded that the efficiency of the electro-deposition remains constant for all the deposits, at least for the deposition times studied.

Second, two straight lines are obtained from the plot of i_p/A versus the electrogeneration charge (Fig. 4). One corresponds to the anodic peak and the other to the cathodic peak. Thus, a good correlation exists between the peak current and the voltammogram charge.

If the peak potential and half-peak width are analyzed, the anodic and cathodic peaks become broader and the peak-to-peak separation increases with the deposited amount. The increasing separation between the anodic and cathodic peaks, and of the half-peak width, with the deposited amount is caused by an ohmic drop effect. If E_p versus i_p is plotted, straight lines are obtained. The slope of these lines is related to the uncompensated resistance mainly due to the ITO electrode.

Finally, if the films are assumed to be totally crystalline, students can estimate the film thickness by the expression that relates the electrogeneration charge to the amount of substance (δ):

$$l = \frac{Q}{A} \cdot \frac{l_0^3 \cdot N_A}{4}$$

where l_0 is the length of the Prussian blue unit cell and has a value of 10 \AA (δ), N_A is Avogadro's number, and A is the electrode area.

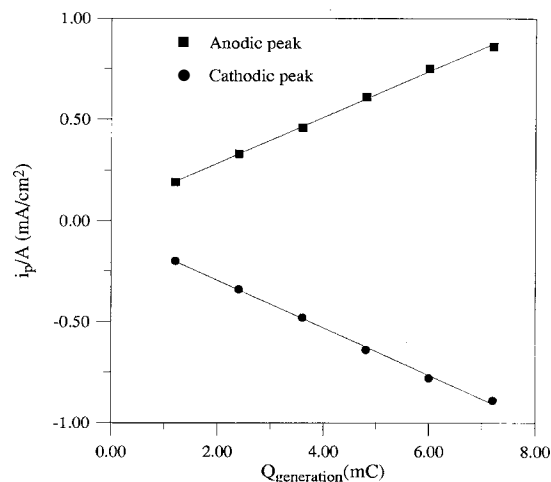


Figure 4. Variation of peak current with electrogeneration charge.

This experiment can be complemented by spectroscopic measurement of PB films in the visible region ($\lambda_{\text{max}} = 690$ nm). The Beer-Lambert law is obeyed; hence the voltammetric results can be compared with the spectroscopic ones to prove the good correlation between the results obtained by means of the two techniques.

The linear relationship between charge or peak current and the amount of deposited PB fails when deposition times are longer because of mass-transport effects through the film, ohmic drop, and the amorphous character of the deposits.

The recommended scan rate is about 20 mV/s. At scan rates faster than 100 mV/s the capacitive effects of the ITO/PB/solution affect the voltammogram shape. Scan rates slower than 20 mV/s can make the experiment too long and also cause low accuracy in the measurement of current. These nonideal effects (ohmic drop, capacitive, and transport), as well as the theoretical interpretation of the voltammogram shape (I), could be studied in specialized courses in electrochemical kinetics or electrochemistry of materials.

As the experiment has been designed, it can be concluded with the acquisition of a single complete voltammogram—for example, $t_d = 150$ s (Fig. 5), in which the color changes of the system should be written down and the standard formal potential E° for each system should be calculated.

It is very important to notice that the color changes occur gradually. This is caused by the variations of the relative proportions of PB, PY, and ES on the ITO electrode. Therefore observation of the gradual color changes is an intuitive way of qualitatively introducing the Nernst equation.

Acknowledgments

J. J. García-Jareño and David Benito acknowledge a fellowship from Generalitat Valenciana, Conselleria d'Educació y Ciència. Part of this work has been supported by CICYT (PTR94-0066).

Literature Cited

1. Neff, V. D. *J. Electrochem. Soc.* **1978**, *125*, 886–887.
2. Dostal, A.; Meyer, B.; Scholz, F.; Bond, A. M.; Marken, F.; Shaw, S. J. *J. Phys. Chem.* **1995**, *99*, 2096–2103. Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism. Fundamentals and Applications*, VCH: Weinheim, 1995; Chapter 6.
3. Itaya, K.; Ataka, T.; Toshima, S. *J. Am. Chem. Soc.* **1982**, *104*, 4767–4772.
4. Mortimer, R. J.; Rosseinsky, D. R. *J. Electroanal. Chem.* **1988**, *151*, 133–147.
5. Kellawi, H.; Rosseinsky, D. R. *J. Electrochem. Soc.* **1982**, *131*, 373–378.
6. Roig, A.; Navarro, J.; Garcia, J. J.; Vicente, F. *Electrochim. Acta* **1994**, *39*, 437–442.
7. Itaya, K.; Ataka, T.; Toshima, S. *J. Am. Chem. Soc.* **1982**, *104*, 4767–4772.
8. Sijerko, L. M.; Kuwaner, T. *J. Electrochem. Soc.* **1983**, *130*, 396–402.
9. Buser, H. J.; Schwarzenbach, D.; Petter, W.; Ludi, A. *Inorg. Chem.* **1977**, *16*, 2704–2710.
10. Aoki, K.; Tokuda, K.; Matsuda, H. *J. Electroanal. Chem.* **1983**, *146*, 417–424.

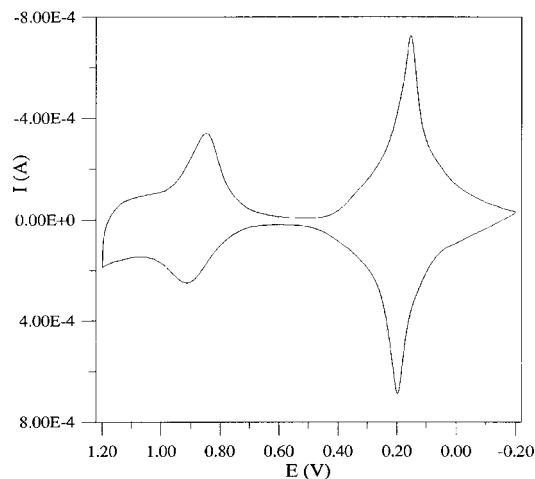


Figure 5. Complete CV of Prussian blue films on ITO electrode. All potentials referred to Ag/AgCl/1 M KCl.