

Chronocoulometric Study of the Electrochemistry of Prussian Blue

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During the electrochemical oxidation of Prussian blue (PB) to Prussian yellow (PY), an electrocatalytic oxygen production proceeds at the electrode when aqueous electrolyte solutions are used. The formed oxygen is scavenged by the PY, probably by absorption, and it is consumed during the electrochemical reduction of PY to PB by a heterogeneous chemical reaction of PB with oxygen to PY and hydrogen peroxide. Because of this catalytic regeneration of PY, it is impossible to determine the amount of low-spin iron by chronocoulometry using a potential program in which PB is first oxidized to PY and then the charge is measured to reduce PY to PB. The latter charge is biased by the electrocatalytic PY regeneration.

Introduction

Since the early report of V. D. Neff that iron(III) hexacyanoferrate(II) (Prussian blue, PB) can be synthesized as a film on solid electrodes,¹ this compound has been studied extensively by electrochemical and other physicochemical techniques. The importance of Prussian blue and its analogues, that is, the metal hexacyanoferrates (Mhcf, where M = Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, etc., and hcf = hexacyanoferrate), is related to its electrochromic^{2–4} and electrocatalytic⁵ properties and its potential for applications in sensors, batteries,⁶ and so forth. Mhcf's possess a zeolitic structure in which the M ions are coordinated to the nitrogen of the CN[−] ions and the hcf moiety form a 3D structure.⁷ Upon oxidation of the carbon-coordinated low-spin Fe(II) ions of the hcf, cations are leaving the film in order to maintain electroneutrality.⁸ The electrochemical features and thermodynamic aspects⁷ of this process have been described previously. In the particular case of PB, two redox processes take place. The redox process at more negative potentials is caused by the iron coordinated to nitrogen (i.e., the high-spin iron), and the other corresponds to iron coordinated to carbon (i.e., low-spin iron). Another Mhcf that exhibits two redox processes is, for example, Cohcf.⁹

Both redox processes of PB involve the exchange of cations, usually monovalent alkali metal ions, between the solid compound and the solution: the expulsion of these cations from the Mhcf lattice to the solution during oxidation and their uptake during reduction. This typical insertion electrochemistry, observed for all Mhcf compounds, plays a role in trials to make batteries⁶ and in analytical applications.¹⁰

Although Prussian blue has been studied so extensively, it is highly surprising to see that no coulometric study of the two electrode processes, that is, that of the high-spin and the low-spin iron, has been published so far. This is so surprising especially because one might expect to be able to determine the ratio of high-spin to low-spin iron in PB in experiments.

However, in experiments carried out in our laboratory with both electrochemically and chemically synthesized PB (the latter using the abrasive transfer technique¹¹), the coulometric data of both process are in disagreement with the structure and stoichiometry of PB. In fact, considering a 1:1 stoichiometry for low-spin iron to high-spin iron, the charge ratio between the anodic and cathodic redox processes should be equal to unity. In the experiments, however, this ratio is in excess of 1 for aqueous media, independent of the electrochemical technique employed (cyclic voltammetry or chronocoulometry). Here, we report potentiodynamic and potentiostatic measurements that allow proposing a simple model to explain these facts.

Experimental Section

The electrochemical measurements were performed employing a conventional electrochemical cell with three compartments. The working electrode was prepared using a 5-mm diameter graphite paraffin-impregnated electrode (PIGE) according to the procedure described previously.^{11,12} The working electrode was rubbed gently on the chemically synthesized solid PB to transfer small amounts of the sample to the electrode surface. A Ag/AgCl electrode (saturated with KCl, $E = 0.197$ V vs NHE) was employed as the reference electrode, and a platinum wire (0.5 cm²) was used as the auxiliary electrode. All of the electrochemical experiments were performed with either a Zahner IM6e or an AUTOLAB (ECO-Chemie, Netherlands) potentiostat–galvanostat. Data acquisition and data analysis were carried out using a THALES package from Zahner Elektrik GMBH & Co. The experiments were performed at room temperature and under inert atmosphere employing analytical reagents (Sigma-Aldrich), which were used without further purification. PB was synthesized according to the following procedure. FeCl₂·4H₂O (3.97 g) was dissolved in 100 mL H₂O, 1.1 g Fe powder was added, and the solution was boiled under reflux for about 5–10 min. After cooling, the solution was filtered and purged with nitrogen for another 10 min. K₄Fe(CN)₆·3H₂O (8.44 g) and KNO₃ (4.04 g) were dissolved in 100 mL of water, and this solution was also purged with nitrogen for 10 min. The first solution was added dropwise to the second

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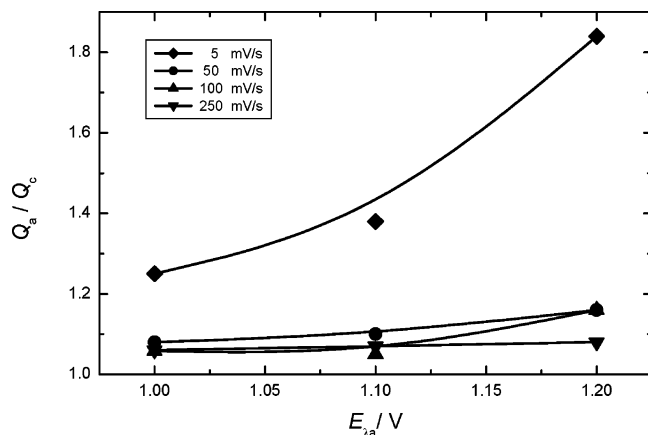


Figure 3. Plot of Q_a/Q_c charge ratio of low-spin iron versus $E_{\lambda a}$ at different scan rates.

the previous potentiodynamic cycle ($n - 1$). This behavior is observed from the fifth cycle onward. Therefore, the charges are always decreasing with the number of cycles. Besides, when a potentiostatic pulse (-0.1 V) was applied to the electrode for five minutes, after n potentiodynamic cycles, the anodic charge of the first cycle was re-established. One way to understand the facts described previously could be a slightly slower reduction process in comparison to the oxidation process of the high-spin iron. This slower process could be the electron transfer at the graphite/hcf interface, the ion transfer at the solution/hcf interface, the electron transport inside the hcf (hopping or conduction via conduction bands), or the ion transport (diffusion) inside the hcf.¹⁵ The ion transport in the solution cannot be responsible for the above-described fact because the concentration in that phase is very large.¹⁶

Analysis of the Charges Associated with the Low-Spin Iron (LSI). When a similar analysis is carried with respect to the *low-spin* iron of the PB, considering a stabilized voltammogram showed in Figure 1C, the Q_a/Q_c charge ratios were always greater than unity also, but the corresponding values were dependent on both the scan rate and the anodic limit ($E_{\lambda a}$) of the potentiodynamic cycles. This is demonstrated in Figure 3 for data obtained from cyclic voltammograms measured at different scan rates and different $E_{\lambda a}$ values.

According to Figure 3, the major difference found between Q_a and Q_c occurs when the potentiodynamic experiments are performed at lower scan rates and when the $E_{\lambda a}$ values are increased. This behavior can be explained, as already mentioned for the high-spin iron, either as due to slow kinetics of the reduction or due to some side reaction of the oxidized PB. This side reaction can be the oxidation of water to oxygen by oxidized Prussian blue. Figure 4 shows the two components of the anodic signal of low-spin iron as obtained by curve fitting. Here, it is very important to stress that curve 2 in the Figure does not correspond to the blank response of the graphite electrode. Indeed this is much smaller in that potential range, such as that shown in the same Figure as curve 1. Therefore, the process associated with curve 2 (water oxidation mediated by PB) is a component of the electrochemical response of the PB. Later we shall show that this additional response is indeed of catalytic origin.

Further insight into the complex electrochemistry of Prussian blue was obtained from chronocoulometric experiments: In these experiments, the Prussian blue was initially completely reduced at -0.1 V for an extended time, and then the charge for oxidizing the high-spin iron was measured at $+0.4$ V. This charge reached a constant value (cf. Figure 5). However, when

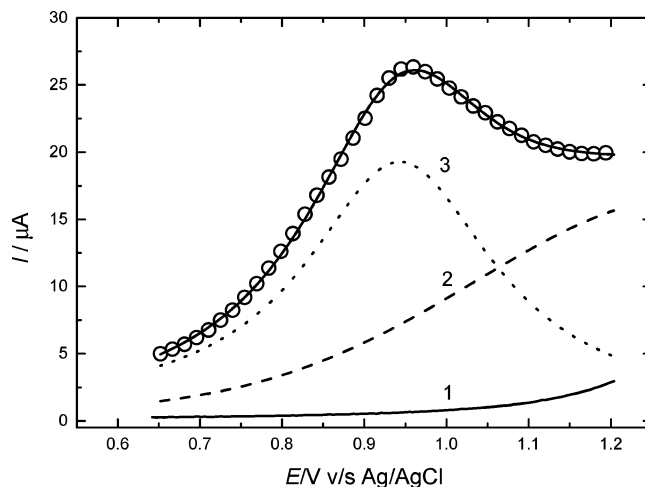


Figure 4. The overall current in the potential range from 0.65 to 1.2 V signals: fitted I/E data (solid line), and experimental data (open circle). Curves 2 and 3 correspond to the processes associated with PB. Curve 1 corresponds to the I/E response for an uncoated graphite electrode in the working electrolyte. Scan rate: 0.05 V s^{-1} .

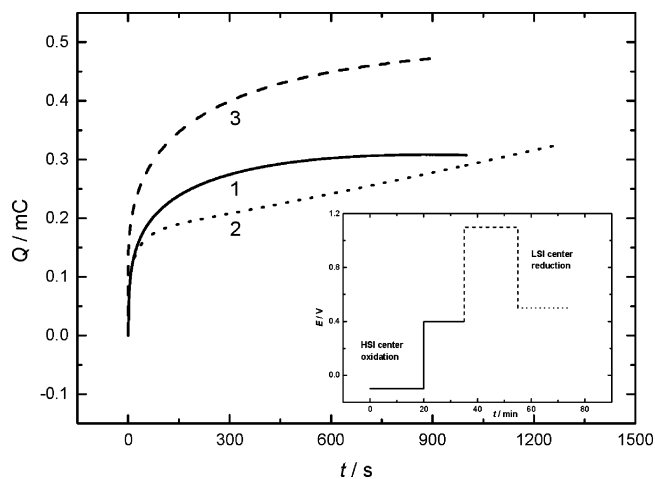
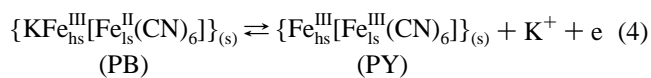


Figure 5. Chronocoulograms of PB. (1) Oxidation charge for high-spin iron of completely reduced PB at the potential -0.1 V. (2) Reduction charge for low-spin iron of completely oxidized PB at the potential 1.1 V. (3) Oxidation charge for low-spin iron at the potential 1.1 V. The inset shows the potential–time program. Electrolyte, $1 \text{ mol L}^{-1} \text{ KNO}_3$.

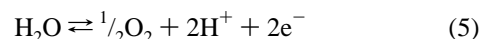
the Prussian blue was initially completely oxidized at a potential of $+1.1$ V, and the charge for reduction of the low-spin iron was measured at $+0.5$ V, that charge did not reach a constant value (cf. Figure 5), although the voltammogram according to Figure 1 does not show any possible interfering process at the reduction potential of $+0.5$ V.

The coulometric results can be explained assuming the following two simultaneous processes at $+1.1$ V:

(i) oxidation of low-spin iron centers



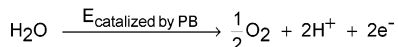
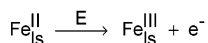
(ii) water oxidation



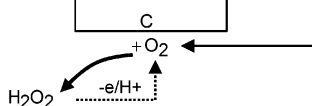
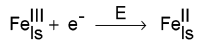
where (s) denotes solid phases and PY represents Prussian yellow.

SCHEME 1 : Chemical and Electrochemical Reaction that Avoids Reaching a Constant Charge for Low-Spin Iron Reduction

During Oxidation at 1.1 V.



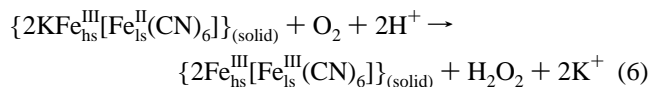
Reduction at 0.5 V
(following the previous oxidation)



Process ii must be the result of electrocatalysis in the sense that PB decreases the oxygen evolution overpotential. In fact, the current corresponding to the water oxidation observed on the uncoated graphite electrode (curve 1 in Figure 4) is smaller than the assumed electrocatalytic curve (curve 2 in Figure 4). It is important to note that the oxygen produced remains in the PB structure. Therefore, all of the processes that will be mentioned below take place inside of the PB film.

When a reduction pulse is applied (0.5 V) following the oxidation of the low-spin iron, reaction 4 is reversed and PB is regenerated. According to our hypothesis, the PB is partially reoxidized to PY by the oxygen present in the system. In turn, the oxygen is most probably reduced to hydrogen peroxide. Next, the PY is electrochemically reduced back to PB. However, the hydrogen peroxide can be electrochemically oxidized back to oxygen. The diffusion of hydrogen peroxide toward the solution was rejected by means of ring-disk experiments because no current was detected in the ring at a potential of 0.5 V. The additional reduction charge measured at 0.5 V for the reduction of PY occurs because iron(III) is regenerated in a chemical reaction of low-spin iron(II) with oxygen present inside the film. The above is represented by Scheme 1. Thus, a cycle of chemical and electrochemical reactions occurs, and therefore a constant cathodic charge value corresponding to the electroreduction of PY cannot be attained. From a thermodynamic point

of view, the heterogeneous chemical reaction between PB and oxygen represented by eq 6



is possible because the standard free energy has a negative value. From the formal potential of Prussian blue¹⁷ and the standard potential of oxygen/hydrogen peroxide,¹⁷ the standard free energy, ΔG^\ominus , of reaction 6 can be calculated to be $-197.7 \text{ KJ mol}^{-1}$. It is important to stress that the standard Gibbs energy of the oxidation of low-spin iron in solid Prussian blue is more negative than the same reaction for hexacyanoferrate ions dissolved in water by $166.6 \text{ KJ mol}^{-1}$! The much higher driving force of the reaction of oxygen with solid hexacyanoferrate makes it very easy to understand that this reaction is more important for solid hexacyanoferrates than for aqueous solution systems. When coulometric experiments were performed in electrolyte solutions saturated with oxygen, under different hydrodynamic conditions (data not shown), no changes of the coulometric behavior of the above-described low-spin iron were observed. This can be understood assuming that the amount of oxygen produced during the oxidation period at the potential imposed is rather large and probably remains absorbed inside of PY.

To test the hypothesis that oxygen is electrocatalytically formed from water and that the produced oxygen drives the cycles shown in Scheme 1, we have performed experiments in two nonaqueous media: (i) 55 mM KCl in methanol and (ii) 1.3 mM KPF₆ in acetonitrile. In both systems, water activity was kept at very low levels to avoid the presence of oxygen in the system. Figure 6 shows the cyclic voltammograms of PB obtained in methanol and acetonitrile electrolytic media.

In both systems, the electrochemical processes of high-spin and low-spin iron centers are clearly observable, but the peak currents are smaller and more drawn out (ohmic effect) than those in the case of aqueous electrolyte solutions (see Figure 1). In both systems, the ratio between the anodic and cathodic charges are as follows: $Q_{a1} < Q_{c1}$ and $Q_{a2} > Q_{c2}$. However, when the blank currents were subtracted (not shown) the ratios of total anodic to total cathodic charges were close to unity. The voltammetric responses in these media show that the electroreduction processes of the low-spin iron are kinetically rather slow, that is, they are indeed incomplete at the cathodic

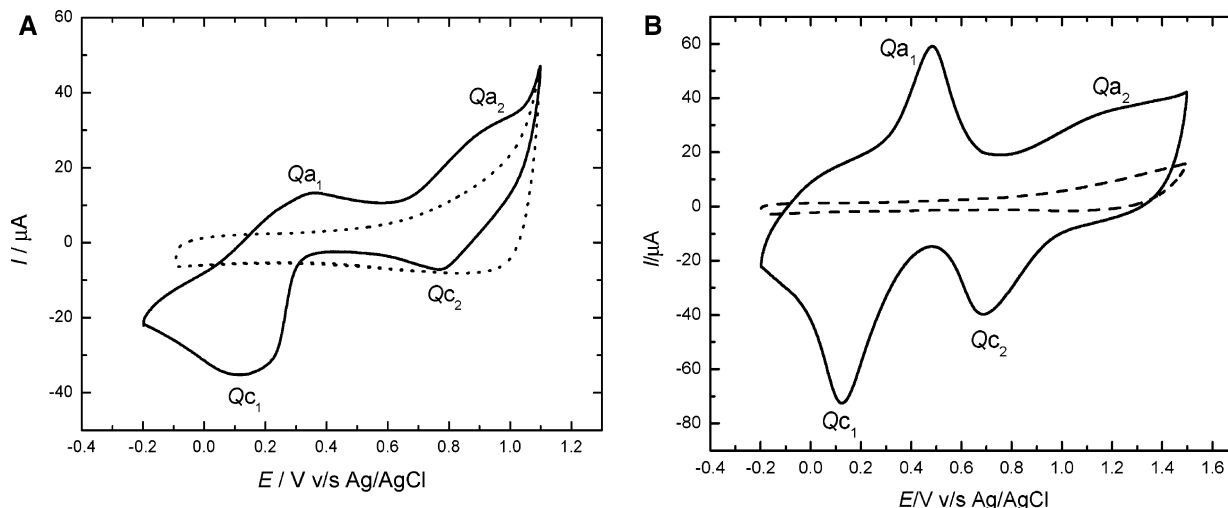


Figure 6. Cyclic voltammograms of PB in two nonaqueous electrolyte media (A) 55 mM KCl in methanol (.....) graphite and (—) PB attached to graphite electrodes. (B) 1.3 mM KPF₆ in acetonitrile (---) graphite and (—) PB electro-synthesized on graphite. Scan rate: 0.05 mV s^{-1} .

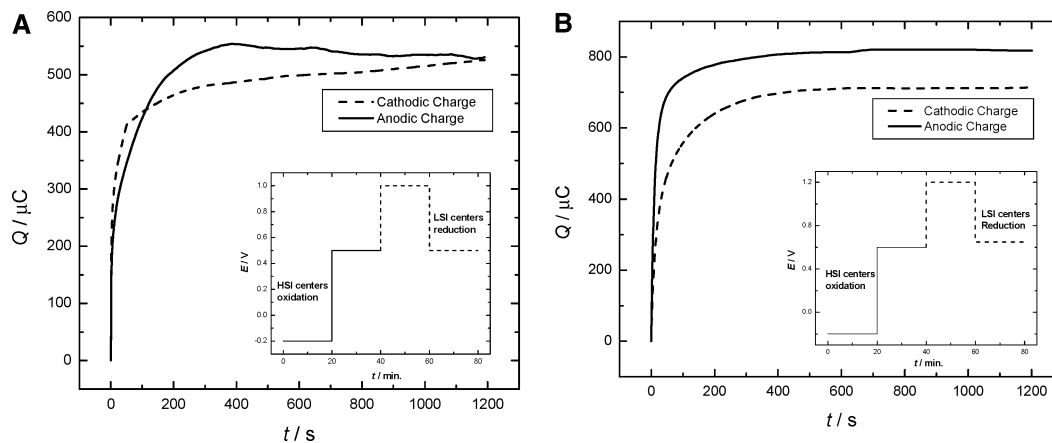


Figure 7. Chronocoulograms showing the anodic (solid line) and cathodic (dashed line) charge variation of high-spin and low-spin iron centers in PB when measured with the potential programs shown in the insets. Electrolytes: (A) 55 mM KCl in methanol, (B) 1.3 mM KPF₆ in acetonitrile. Inert atmosphere.

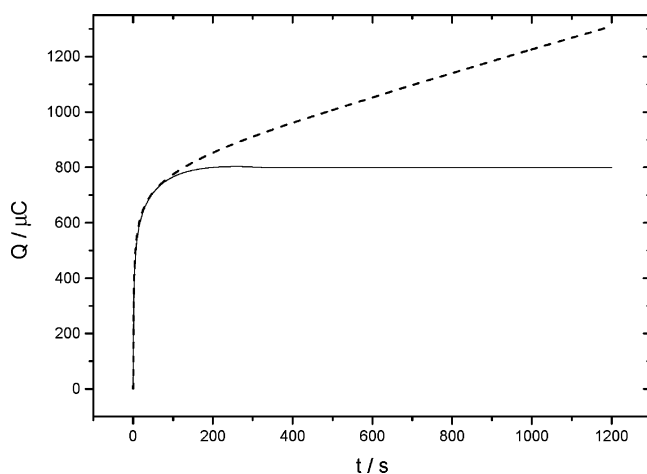


Figure 8. Chronocoulograms showing the anodic (solid line) and cathodic (dashed line) charge variation of high-spin and low-spin iron centers in PB. Electrolyte: 1.3 mM KPF₆ in acetonitrile, oxygen atmosphere (1 atm). The E/t program applied is showed in the inset of Figure 7.

peaks of the low-spin system, and the complete reduction of the low-spin iron seems to take place underneath the cathodic peaks of the high-spin system.

Chronocoulometric studies of PB with electrolyte solutions in methanol and acetonitrile, which were performed with analogous potential programs as in the case of aqueous electrolytes, showed in both cases that the anodic charge, Q_a , consumed by oxidation of the high-spin iron centers, and the cathodic charge, Q_c , consumed by the reduction of previously oxidized low-spin iron centers reach constant values (cf. Figure 7). This is very different from what was observed with aqueous electrolytes and what was interpreted in Scheme 1.

The differences between the aqueous and nonaqueous electrolytes are easily understandable because the latter cannot provide the oxygen to drive the reaction cycles given in Scheme 1. Nevertheless, when the same experiment was performed in acetonitrile media saturated with oxygen, the chronocoulogram obtained (Figure 8) is very similar to those obtained in aqueous media shown previously in Figure 5. In the present case, the oxygen that saturates the solution penetrates into the PB film and therefore the same cycled reaction presented in Scheme 1 take place.

Conclusions

This study shows that the electrochemistry of Prussian blue using aqueous electrolyte solutions is much more complex than it has been believed to be so far. For the first time, it could be shown that an electrocatalytic oxygen formation is prompted by the presence of solid Prussian blue on the electrode surface. The production of that oxygen is unavoidable with aqueous solutions, and this oxygen reacts in a very slow heterogeneous reaction with low-spin iron(II) when that was formed by reduction of Prussian yellow. The back-oxidation of low-spin iron(II) fuels a reduction current that is constant for hours. This can be understood only if the oxygen produced during the PB to PY oxidation step is available at the electrode for such long times. Therefore, it must be assumed that the oxygen is strongly retained in the Prussian yellow. That is possible because elemental oxygen is an uncharged molecule and therefore is not efficiently removed from the PB as the counterions are during the oxidative processes of PB. Prussian yellow has a very large surface area, and the PY and PB morphology is such that the small crystallites form spongelike structures that may effectively keep large amounts of oxygen, where large is meant with respect to the rather small rate of reaction 6 that does not consume much oxygen per time unit. Because reaction 6 is unavoidable with aqueous electrolyte solutions, it is impossible to determine the true ratio of high-spin iron to low-spin iron by measuring the amount of high-spin iron by reduction of Everitt's salt to Prussian blue and the amount of low-spin iron by measuring the charge consumed by reduction of Prussian yellow to Prussian blue. In principle, these two reactions would lend themselves for that purpose because the reduction of Prussian blue to Everitt's salt and the oxidation of Prussian blue to Prussian yellow are always biased by accompanying currents. In the case of oxidation of PB to PY, this is the electrocatalytic oxygen formation discussed in this paper with respect to the effect the produced oxygen has on the current observed in the back-reduction of PY to PB. The irreversible side reactions involving water described in this communication give the explanation that trials to use solid metal hexacyanoferrates in batteries always showed a decreasing efficiency.⁶ The results obtained here may suggest that batteries with nonaqueous electrolytes may provide better results; however, the generally inferior voltammetric behavior (see Figure 6) does not give much hope, at least for rocking chair batteries involving both the high- and low-spin systems.

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