Notes

Electron-transfer Processes and Electrodeposition involving the Iron Hexacyanoferrates studied Voltammetrically

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Iron(III) hexacyanoferrate(II) (' Prussian Blue ') is shown voltammetrically to deposit from a solution of Fe^{3+} and hexacyanoferrate(III) by two dominant electroreductions. The progenitor species is probably the 1 : 1 complex which diffuses to the electrode. Reoxidation is only partly achieved, to ' Prussian Green ' (PG), also occurring in two forms. The composition of PG, as containing $[Fe^{III}(CN)_6]_3[Fe^{II}(CN)_6]_4$, is confirmed coulometrically and mechanistic detail is clarified.

The iron hexacyanoferrates [1-3] (Table 1) form thin films on conductive metals,[3-5] particularly by spontaneous or electrochemical reduction [3,6] of iron(III) hexacyanoferrate(III) in solution to deposit ' Prussian Blue ' (PB) film. Bulk PB has been studied as regards its structure,[7,8] spectra,[9,10] magnetic susceptibility,[11] Mössbauer spectra,[12] and ion exchange of the Fe^{3+} or M^+ counter cation.[13-15] Conversions to other oxidation states which in principle can be effected in bulk are best studied electrochemically in thin films,[3,5,6] on Pt, for example.

Experimental

A Bruker E44S polarograph was used with a 1 cm^2 platinum working electrode, of a size amenable to visual examination of deposits. A platinum wire counter electrode and saturated calomel electrode were used in a glass vessel. The working electrode was washed in aqua regia, anodised and cathodised in 0.5 mol dm^{-3} sulphuric acid for 30 s at 0.19 mA, then washed copiously with distilled water. Solutions of BDH or Hopkin and Williams analytical grade $Fe_2(SO_4)_3$ and $K_3[Fe(CN)_6]$ were used. Voltammograms were run on fresh mixtures, or the single solutions, of the following compositions of Fe^{3+} and $[Fe(CN)_6]^{3-}$ respectively: (a) 0.03 + 0.0025 mol dm^{-3}; (b) 0.015 + 0.0025 mol dm^{-3}; (c) 0.01 + 0.005 mol dm^{-3}; (d) 0.005 + 0.015 mol dm^{-3}. A mixture of lithium perchlorate (0.2 mol dm^{-3}) and perchloric acid, to give pH 2, was the supporting electrolyte. Single-cycle voltammograms for mixtures (a)—(d) as well as the component-ion {Fe^{3+} and $[Fe(CN)_6]^{3-}$} solutions are shown in Figure 1. At appropriate points in subsequent experiments the electrode was removed for examination of colour of the deposit before, during, and after each peak.

Results and Discussion

Possible Mechanisms of Deposition of PB.—Since, in a suitable cell, electroreduction of $Fe^{III}[Fe^{III}(CN)_6]$ in solution ultimately to PB_{film} could proceed by a number of mechanisms, each if operative giving a current flux at a potential determined by the nature of the participant species on the electrode surface, voltammetry provides an excellent tool for selecting the mechanisms. The main possibilities are given below.

(1) Fe^{3+} or $[Fe(CN)_6]^{3-}$ is reduced, either (a) then to react with a PB-forming partner to give colloidal PB subsequently depositing or (b) to deposit directly as PB_{film} on the electrode. Processes such as (a) and (b) will in general occur at different potentials (see preceding paragraph).

(2) $Fe^{3+}[Fe(CN)_6]^{3-}$ complex is reduced as an entity either (a) in solution as $PB_{colloid}$ subsequently depositing, or (b) on the electrode surface, to form PB_{film} directly on the Pt.

(3) (a) The product, *e.g.* PB_{film}, appearing in more than one chemical or physical form will give rise to the corresponding extra potentials for current enhancement [*i.e.* extra cyclic voltammogram (c.v.) peaks]. (b) The same contention applies to reactants.

Thus c.v. on mixed Fe^{3+} + $[Fe(CN)_6]^{3-}$ solutions (accompanied by visual examination of deposits), compared with voltammetry on separate solutions of Fe^{3+} and $[Fe(CN)_6]^{3-}$, to assign contributions of individual ions in the mixture c.v., has now been used to choose from (1)—(3).

Side Issues Resolved.—(*i*) $[Fe(CN)_5(OH_2)]^{2-}$ (ref. 15), possibly present from hydrolysis of $[Fe(CN)_6]^{3-}$, was shown in separate experiments to form PB but only in suspension, not as PB_{film}.

(*ii*) Aged, slightly acid $[Fe(CN)_6]^{3-}$ solutions turn greeny

Table 1. Iron hexacyanoferrates

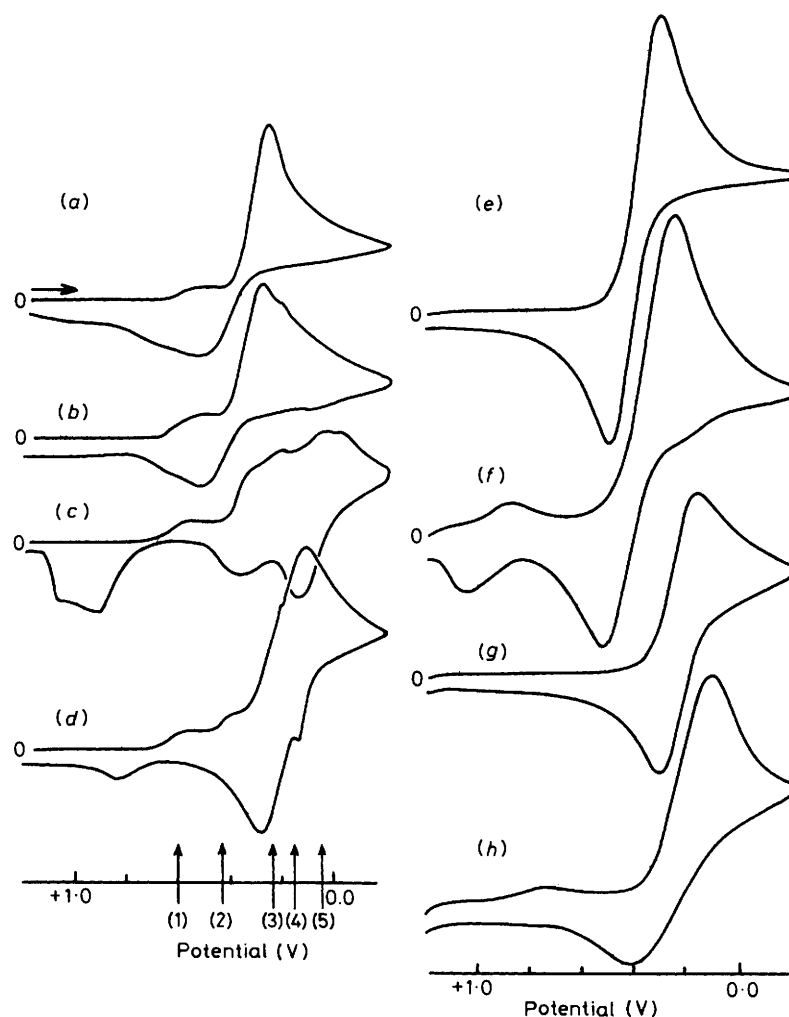| Trivial name	Abbreviation	Idealised formula	Comment	Ref.
Soluble Prussian Blue	PB	$KFe^{III}[Fe^{II}(CN)_6]$	Peptisable	1
Insoluble Prussian Blue	PB	$(Fe^{III})_4Fe^{III}[Fe^{II}(CN)_6]$	Unpeptisable	1
Prussian Brown	PX	$Fe^{III}[Fe^{III}(CN)_6]$	Reactive oxidant	2
Prussian Green	PG	$\{[Fe^{II}(CN)_6]_x[Fe^{III}(CN)_6]_{2x}\}^{10x-}$	$x = \frac{1}{3}$ (?)	2,3
Prussian White	PW	$K_2Fe^{II}[Fe^{II}(CN)_6]$	Reactive reductant	2

Figure 1. Voltammograms of (a)—(d) mixtures and (e)—(h) single-ion solutions; (f) and (h) are for a thin film of PB on Pt. [Fe^{3+}] and [Fe(CN)$_6^{3-}$] are respectively (a) 0.030 and 0.0025 mol dm^{-3}; (b) 0.0150 and 0.0025 mol dm^{-3}; (c) 0.010 and 0.0050 mol dm^{-3}; (d) 0.0050 and 0.0150 mol dm^{-3}; (e) and (f) 0.010 mol dm^{-3} Fe^{3+}; (g) and (h) 0.005 mol dm^{-3} [Fe(CN)$_6$]$^{3-}$. Scan rate 5 mV s^{-1}; potentials are versus s.c.e. Cathodic formation of (1) PB, (2) PB, (3) Fe^{2+}, (4) [Fe(CN)$_6$]$^{4-}$, and (5) PW is shown by the numbered arrows

yellow (probably PG$_{colloid}$ but see ref. 16) but react electrochemically as do fresh solutions, provided no actual suspension is evident.
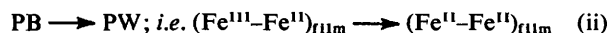
(iii) Will PB$_{film}$ already present affect electrode reductions of (individual) Fe^{3+} or [Fe(CN)$_6$]$^{3-}$? To answer this, voltammograms of these individual reductions have been run with [Figure 1(f) and (h)] and without [Figure 1(e) and (g)] thin PB$_{film}$ on the Pt; only slight understandable peak shifts are produced. Such shifts, due to potential drop through PB$_{film}$, and so being variable because they depend on the adventitious film thickness, introduce no uncertainty in interpretation.

(iv) The observation that on reoxidation of PB only PG not PX is retrieved, allows coulometric ratio measurements to establish the composition of PG. Thus voltammogram areas (by weighing, and proportional to coulombs) for Fe^{3+} + [Fe(CN)$_6$]$^{3-}$ ⟶ PW, and then for PW ⟶ PG, gives for these respective processes (detailed later) 0.58 ± 0.03 : 0.42 ± 0.03, PB$_{film}$ effects determining the limits. The composition given in Table 1 for PG requires a ratio of 2 : 1⅓ (0.55 : 0.45) for the two processes, and is thus now independently supported by coulometry.

Cathodic Scans.—In mixtures, decreasing the stoicheiometric ratio [Fe^{3+}] : [Fe(CN)$_6^{3-}$] from 12 : 1 to 1 : 3 gives at first increasing complexity in going from Figure 1(a) to (d). By referring to the single-ion scans, Figure 1(e) and (f), and observing the colour changes, assignments can be made to each reduction peak with confidence, and such assignments to, e.g. the multi-peaked Figure 1(c) with a 2 : 1 ratio, are found to apply throughout, with small potential shifts as discussed above. Thus in Figure 1(c) the first two cathodic peaks at 0.55 V and 0.35 V are assigned to the process (i),

$$(Fe^{III}-Fe^{III})_{soln} \longrightarrow PB_{film} \qquad (i)$$

followed by Fe^{3+} reduction (0.22 V) and that of [Fe(CN)$_6$]$^{3-}$ (0.06 V). In conditions as for Figure 1(c) the final reduction at −0.02 V, process (ii), is clearly evident from the colour

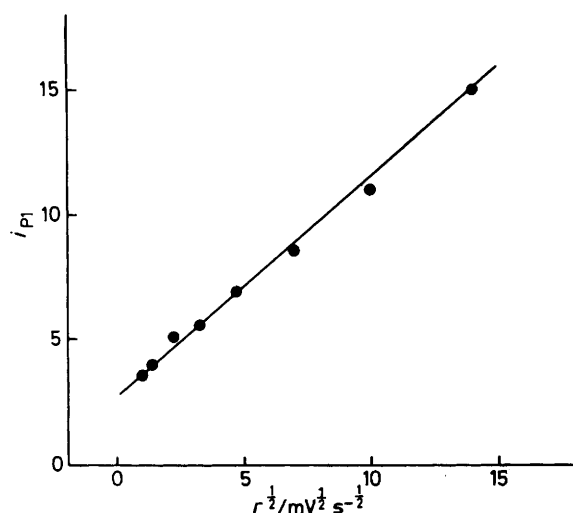$$PB \longrightarrow PW; i.e. (Fe^{III}-Fe^{II})_{film} \longrightarrow (Fe^{II}-Fe^{II})_{film} \qquad (ii)$$

change, which is more obscure under all other conditions. The reductive sweep thus provides three possible processes for formation of PB, the extra one resulting from the possi-

Table 2. Peak currents at 0.55 V (i_{p1}) and ca. 0.35 V (i_{p2}) (arbitrary units) and concentrations of possible electroactive species

Solution	i_{p1}	i_{p2}	$10^3[Fe^{3+}]$ [a]/ mol dm^{-3}	$10^3[Fe(CN)_6^{3-}]$ [a]/ mol dm^{-3}	$10^3[Fe^{3+}Fe(CN)_6^{3-}]$ [a]/ mol dm^{-3}
(a)	10	125	29	1.6	0.9
(b)	8	52	14	1.9	0.6
(c)	9	28	9	4	0.8
(d)	8	6	3	14	0.8
(j) [b]	18	132	25	10	5

[a] Calculated from K = 20 dm^3 mol^{-1}. [b] Fe$_2$(SO$_4$)$_3$ (0.015 mol dm^{-3}) + K$_3$[Fe(CN)$_6$] (0.015 mol dm^{-3}).

Figure 2. Plot of the first peak current, in arbitrary units, versus (sweep rate)$^{\frac{1}{2}}$. Concentrations are as in Figure 1(c)

bility of the electroreduced Fe^{2+} ions reacting with [Fe(CN)$_6$]$^{3-}$ at the electrode, but as no PB is seen liberated to the solution, the extent of this is clearly rapidly limited by the almost immediate further cathodic removal of [Fe(CN)$_6$]$^{3-}$ by its reduction to [Fe(CN)$_6$]$^{4-}$. {The [Fe(CN)$_6$]$^{4-}$ cannot precipitate as PB here since at such potentials no Fe^{3+} exists at the electrode.}

Anodic Scans.—Before dealing with the later mixtures [Figure 1(c) and (d)], Figure 1(a) and (b) can be viewed in total, by comparison with Figure 1(e), as Fe^{2+} $\rightleftharpoons$ Fe^{3+} slightly modified by processes involving PB. Figure 1(c) shows PW $\longrightarrow$ PB starting at ca. 0.1 V; Figure 1(d) has this process (subdued) at >0.1 V and the cathodically-produced [Fe(CN)$_6$]$^{4-}$ reoxidised at 0.37 V, and this reoxidation also appears in 1(c), but shifted, much as in Figure 1(h) compared with 1(g).

The final anodic processes give products differing from the starting species (Fe^{III}–Fe^{III}). The 0.92 V wave gives PB$_{film}$ $\longrightarrow$ PG$_{film}$, both species adherent, but the second is for PB$_{film}$ $\longrightarrow$ PG$_{colloid}$ where the latter leaves the film as an observable green effluent. To confirm this observation, a voltammogram taken between the now restricted limits 1.2 V to +0.50 V, giving on reduction the first peak due to formation of PB alone, shows also only *one* oxidation peak; a cycle taken to the more negative limit, 1.20 to 0.30 V, i.e. substantially into the second peak, gives *two* oxidation peaks on the reversed part of the cycle. The second of these oxidation peaks again is accompanied by liberation of the green colouration, probably again colloidal PG. Thus PG like PB appears to comprise ' soluble ' and ' insoluble ' forms, though

it is not clear why only one PG-forming peak survives in Figure 1(d).

Second and Further Cycles.—At the end of a cycle unpeptised PG remains on the electrode and a second cycle introduces a new peak for PG $\longrightarrow$ PB between 0.7 and 0.9 V, like those appearing in Figure 1(f) and (h). Further cycling leaves the electrode covered with more and more iron hexacyanoferrate film on which the peak due to the deposition of PB and the free-ion peak become progressively less prominent, and ultimately only the reproducible cycles [6] for the adherent film material survive, as found [6] for film in the absence of congenerions in solution. Other work [17] has shown that the film grows to a maximum of $\lesssim$2 000 Å thick due to the self-limitation of increasing resistance. The single-ion scans on PB-covered electrodes [Figure 1(f) and (h)] had thus to be run on very thin films of PB, to allow for sufficient electron migration.

The Two PB-forming Peaks.—The final question relates to the nature of the two reduction peaks for formation of PB from Fe^{3+} + [Fe(CN)$_6$]$^{3-}$. The height of the first is proportional to $r^{\frac{1}{2}}$ (r = scan rate), Figure 2, and follows the sequence of concentrations of the complex Fe^{III}[Fe^{III}(CN)$_6$] calculated from the formation constant of 20 dm^3 mol^{-1},[18] Table 2. This value gives an overestimate in view of the neglected sulphate complexes, but in Table 2, neither Fe^{3+} nor [Fe(CN)$_6$]$^{3-}$ concentration, free or stoicheiometric, shows any correlation; the presence of sulphate has been deemed useful for the deposition of good quality PB.[6] The second formation peak of PB is not open to an examination of the r dependence since it is a shoulder only poorly resolvable from the free Fe^{3+} peak. The second peak increases with [Fe^{3+}] up to a limit, in contrast with the first. Careful examination shows that the rise to the first peak in fact produces PG, only the plateau onset giving PB. Holding the potential at *less* than the plateau value, i.e. within the range where PG is formed, results in the transformation of PG to PB. The observation accords with that in the previous section: PG if present at the start of the cathodic scan, would actually yield PB earlier than the peaks for electrodeposition of PB.

The possibilities given below exist for the two formation peaks of PB, given in order of decreasing probability.

(*i*) Two forms, soluble and insoluble, of PB are deposited. The corresponding *oxidations* give two forms of PG, as noted above. The [Fe^{3+}]-dependent increase of the second peak might imply its correspondence with formation of the insoluble variety; the limit accords with the observation of the [Fe^{3+}] dependence of direct precipitation.[1]

(*ii*) The first peak might represent formation of PB from the Fe^{III}[Fe^{III}(CN)$_6$] complex as in (*i*), but the second, PB deposition from a different complex containing in addition a sulphate or a further Fe^{3+} ion, or from a sol of Fe^{III}[Fe^{III}(CN)$_6$]. Removal and cleaning of the electrode, after the cathodic scan only, results in small but unequivocal decreases

in the second peak, on successive cathodic scans, in accord with sol removal; the solution does show Tyndall scattering [thus (*i*) and (*ii*) may not be mutually exclusive].

(*iii*) The two peaks correspond to reduction of two configurations of the electroactive species $Fe^{III}[Fe^{III}(CN)_6]$ on the electrode.

Conclusions

Fe^{3+} reduction [3] or $[Fe(CN)_6]^{3-}$ reduction, in mechanism (i) above, can clearly be excluded, and the $[Fe^{3+}Fe(CN)_6^{3-}]$ dependence together with the approximate $r^{\frac{1}{2}}$ dependence of the first PB-producing peak favours a diffusion of the complex as current-determining. The nature of the immediate product is not so clear, PG as film perhaps being implicated, the first maximum corresponding to actual formation of PB. Possibilities for the second peak are given in (*i*)—(*iii*) above. The corresponding anodic processes have been largely clarified, and the composition of PG confirmed.

Acknowledgements

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