Iron Hexacyanoferrate Films: Spectroelectrochemical Distinction and Electrodeposition Sequence of 'Soluble' (K^+-containing) and 'Insoluble' (K^+-free) Prussian Blue, and Composition Changes in Polyelectrochromic Switching

Roger J. Mortimer and David R. Rosseinsky *
Department of Chemistry, The University, Exeter EX4 4QD

Films of Prussian Blue (PB) deposited by electroreduction in the absence of K^+ have absorbance maxima at 730 nm which narrow and shift on voltammetric cycling in KCl solution to 690 nm, these absorptions being deemed diagnostic of 'insoluble' and 'soluble' PB respectively. Spectroelectrochemistry shows that the initial deposit even in K^+ solution is invariably the insoluble form, being then converted into the soluble, irrespective of electrochemical conditions or solution composition; this resolves several problems in the current literature. Electrochemical oxidation of PB gives continuous mixed-valence compositions up to complete oxidation; by contrast, reduction to Prussian White involves clean conversion of one into the other at a critical potential.

Prussian Blue [PB, iron(III) hexacyanoferrate(II)] films have been the subject of intensive study recently.[1-14] The claim [1-3] that PB is electrodeposited, from K^+-containing iron(III) hexacyanoferrate(III) solution, as the 'soluble' form SPB has been contradicted by formulations [8-13] specifying only the insoluble form IPB, the two forms containing K^+ or $\frac{1}{3}Fe^{3+}$ respectively, as the counter cation for solid-phase electroneutrality. Spectroelectrochemical study now establishes clear distinctions between the initially deposited form and that ultimately persisting, and a basis for assignments of the compositions. In a separate study, novel evidence is presented of the contrasting modes of composition change when PB is electrochemically oxidised or reduced.

Experimental

Materials and apparatus were as described previously.[7] Tin oxide–indium oxide (12.5 : 87.5) conducting glass electrodes from English Electric Valve, having a resistance of 20 Ω, 'per square', and 5.5 × 0.9 cm² in size, comprised the working electrodes, on which PB deposits of area *ca.* 0.9 × (3.8 ± 0.1) cm² were obtained by electroreduction of iron(III) hexacyanoferrate(III) solution. Spectroelectrochemistry was conducted in the cell compartment of a Beckman Acta MIV spectrophotometer, with the working electrode transverse in a 1-cm glass optical cell into the top of which were immersed a small laboratory constructed saturated calomel electrode (s.c.e.) and a platinum-wire counter electrode supported by a polytetrafluoroethylene lid, the leads emerging from the cell compartment. The potential of the working electrode was controlled with a PAR 174 potentiostat.

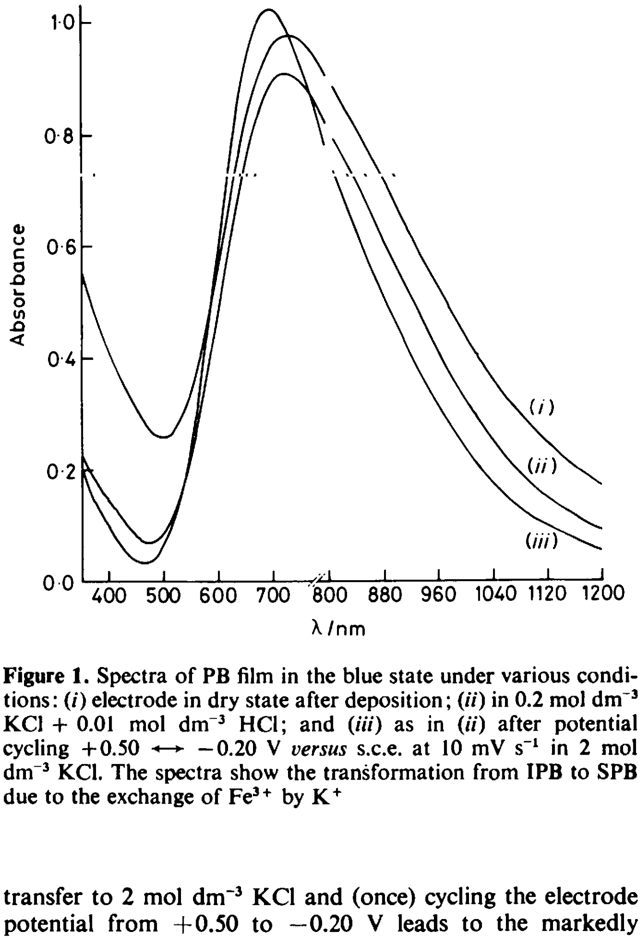

Figure 1. Spectra of PB film in the blue state under various conditions: (*i*) electrode in dry state after deposition; (*ii*) in 0.2 mol dm^{-3} KCl + 0.01 mol dm^{-3} HCl; and (*iii*) as in (*ii*) after potential cycling +0.50 ⟷ −0.20 V *versus* s.c.e. at 10 mV s^{-1} in 2 mol dm^{-3} KCl. The spectra show the transformation from IPB to SPB due to the exchange of Fe^{3+} by K^+

Results and Discussion

Insoluble PB distinguished from Soluble PB.—Earlier voltammetric studies [6,7] of the electroreduction had suggested that there were two reductive processes, at +0.62 and at +0.50 V *vs.* s.c.e., possibly forming IPB and SPB not necessarily in that order. To study IPB alone, a K^+-free solution was made from 5 mmol dm^{-3} $FeCl_3$ and 5 mmol dm^{-3} $[NBu^n_4]_3[Fe^{III}(CN)_6]$ in 0.01 mol dm^{-3} HCl, which gave on electroreduction (using a sodium chloride saturated calomel electrode, *i.e.* a s.s.c.e., to avoid K^+ contamination) a PB film having a broad absorption at 730 nm (top scan, Figure 1, dry film). Transfer to 0.2 mol dm^{-3} KCl + 0.01 mol dm^{-3} HCl gave the slightly diminished second spectrum. Further transfer to 2 mol dm^{-3} KCl and (once) cycling the electrode potential from +0.50 to −0.20 V leads to the markedly narrower band centred at 690 nm (third scan, Figure 1). {The same general observation is obtained on cycling from −0.20 to +1.20 V and back to PB, but loss of film material occurs presumably due to dissolution of $Fe^{III}[Fe^{III}(CN)_6]$ which was therefore avoided in this part of the study.} The shift in the absorbance maximum is assigned to a transformation from $(\frac{1}{3}Fe^{3+})Fe^{3+}[Fe^{II}(CN)_6]^{4-}$ to $K^+Fe^{3+}[Fe^{II}(CN)_6]^{4-}$ on voltammetric cycling, *i.e.* IPB ⟶ SPB, the difference in spectra providing a diagnostic for the forms electrodeposited from any solution.

Since in IPB $(Fe^{3+})_4[Fe^{II}(CN)_6]_3$ has [15] one quarter of the

$Fe(CN)_6$ sites vacant, the mechanism of K^+ uptake on reduction probably involves K^+ occupancy of these (albeit originally anionic) sites, but some K^+ will have to be interstitial if the reduced form Prussian White (PW) is $(K^+)_2Fe^{2+}$-$[Fe^{II}(CN)_6]^{4-}$. (Ludi's[15] inferred absence in IPB of interstitial Fe^{3+} counter cation does not preclude interstitial K^+ in SPB which is clearly less disfavoured on account of its low, 1+, charge.) In addition to the reductive requirement of K^+ uptake, the slightly expanded PW lattice will clearly favour easier ion exchange than occurs with IPB exposed to KCl solution, where negligible transformation to SPB was seen to occur.

Effects of Differing Electrodeposition Conditions on Products.—A constant generating solution of 5 mmol dm^{-3} $FeCl_3$, 5 mmol dm^{-3} $K_3Fe(CN)_6$, 0.2 mol dm^{-3} KCl, and 0.01 mol dm^{-3} HCl was used with a variety of electrochemical conditions as follows: +0.45, +0.50, +0.55, or +0.60 V (*versus* s.c.e.) all for 300 s, or 30 μA for 1 000 s, or 60 μA for 500 s. Although differing efficiencies ensued, in all cases the broad band centred at 730 nm appeared first, then shifted to the lower wavelength with narrowing on potential cycling from +0.50 $\longleftrightarrow$ −0.20 V in 2 mol dm^{-3} KCl. Thus IPB always appears to be initially deposited, but potential cycling *via* PW, in KCl solution, always results in conversion into SPB. Two further checks confirm this. The SPB films when soaked in saturated $FeCl_3$ solution underwent a partial reversion of $\lambda_{max.}$ and broadening, but never completely; the equilibrium, although accessible, is substantially weighted towards SPB. But IPB is *always* formed first, even in an experiment with 3.6 mol dm^{-3} KNO_3, *i.e.* near saturation, with 1 mmol dm^{-3} $FeCl_3$ and 5 mmol dm^{-3} $K_3Fe(CN)_6$.

The unsuitability of the descriptions 'soluble' and 'insoluble' (meaning in fact peptisable and non-peptisable) is emphasised by the former's being the ultimate film form, *i.e.* it is the thermodynamically less soluble. By the same token IPB can be viewed as the 'kinetically insoluble' form: faster flocculation of colloidal material is indeed generally associated with higher charge of the counter ion, and it is presumably just this effect which is responsible for the extra Fe^{3+} incorporation giving the initial IPB.

Comparison with Earlier Work.—The IPB $\longrightarrow$ SPB transformation on cycling explains the origin of the observation[7] that, after electrodeposition at constant potential, the first succeeding cycle in KCl alone differs from the second and all succeeding cycles (Figure 9A and B in ref. 7). This was suggested[7] to arise from structural reorganisation during the first cycle, which is now confirmed as an interchange of counter cations.

Our assignment of spectra resolves the discrepancy between Neff's[1-3] and Itaya's[8-13] views as to the nature of electrodeposited PB. Itaya *et al.*[12] analysed their film and found only traces of K^+, and in consequence assumed all their films to be IPB. Our inferences suggest that these initial analyses were correct. However, their subsequent voltammetry and spectroelectrochemistry were conducted in 1 mol dm^{-3} KCl, which we have shown causes conversion into SPB. Thus interpretations,[12] of oxidation and reduction in 1 mol dm^{-3} KCl solution, solely in terms of IPB, are unlikely to be valid. Neff and co-workers[1-3] on the other hand assert their electrodeposited material to be SPB, and in our view correctly formulate mechanisms in terms of SPB, but they have excluded IPB from consideration as precursor.

These considerations still leave unexplained the two voltammetric peaks[6,7] in electrodeposition of PB from Fe^{3+}-$[Fe^{III}(CN)_6]$ arising at +0.62 and +0.50 V. We have now excluded the first of several suggested[6] alternatives (separate formations of IPB and SPB). While two different species[7] containing $Fe^{III}[Fe^{III}(CN)_6]$ might indeed still be involved, the simplest view must be that only one complex Fe^{3+}-$[Fe^{III}(CN)_6]$ is involved, but the two peaks represent respectively the reductions of Fe^{3+} or $Fe^{III}(CN)_6$ within that complex, either yielding PB.

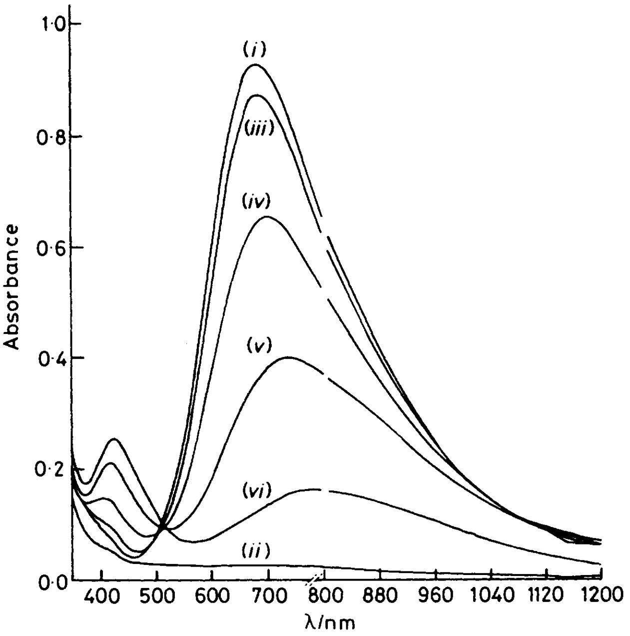

Figure 2. Spectra of PB films at various potentials [(*i*) +0.50, (*ii*) −0.20, (*iii*) +0.80, (*iv*) +0.85, (*v*) +0.90, and (*vi*) +1.20 V (*versus* s.c.e.)] with 0.2 mol dm^{-3} KCl + 0.01 mol dm^{-3} HCl as supporting electrolyte. After electrodeposition, the PB/conducting glass electrode was then cycled in 2 mol dm^{-3} KCl, +0.50 $\longleftrightarrow$ −0.20 V at 10 mV s^{-1}, prior to the spectroelectrochemical measurements described

The Four-colour Electrochromicity: All-oxidised to All-reduced Iron Hexacyanoferrate.—The spectra of the yellow (oxidised, PY), green, blue, and clear ('white') forms of PB and its redox variants are shown in Figure 2, together with two intermediate states between blue and green. The yellow absorption corresponds with that of iron(III) hexacyanoferrate(III) in solution, both maxima being at 425 nm and coinciding with the (weaker) $Fe(CN)_6{}^{3-}$ absorption maximum. Even in the most highly oxidised state a very broad flat band centred at approximately 790 nm persists as a long-wavelength residue of the shifted intervalence absorption. It is absent from $Fe(CN)_6{}^{3-}$ alone and may be assigned to ineradicable traces of $Fe^{II}(CN)_6$ in charge-transfer (c.t.) interaction with Fe^{3+}.

It was of interest that the film composition could be continuously varied between the yellow and blue states by adjustment of the potential. Thus, increase of the potential, from +0.50 V (*vs.* s.c.e.) to more oxidising values, continuously shifts the PB peak originally at 690 nm to longer wavelengths with diminished absorption, while the peak at 425 nm simultaneously steadily increases in absorption presumably due to the increasing Fe^{3+}-$Fe(CN)_6{}^{3-}$ absorption. The reduction of PB to PW is by contrast abrupt, the material transforming to all PW or all PB without pause, depending on the potential set: at potentials less positive than +0.10 V there is complete conversion into PW while at >0.10 V all PB is formed. This difference in behaviour indicates continuous mixed-valence compositions over the blue-to-yellow range (implying no particular uniqueness to the green compositions established by coulometry[6] or spectroscopy[3]) in contrast with the presumably immiscible PB and PW which clearly transform one into the other without intermediacy of composition.

The contrast in behaviour over the ranges PB → PW and PB → PY can be established as follows. The latter involves the introduction of a new $Fe^{II}(CN)_6^{4-}$–$Fe^{III}(CN)_6^{3-}$ mixed-valence system, while the former introduces Fe^{2+}–Fe^{3+} mixed valence. Clearly the former, with the participating iron coordinated at the carbon end of CN^- favourable to bonding and an accompanying expansion of iron-based orbitals, will allow of an extra dimension of mixed-valence delocalisation stabilising the PB → PY range of compositions. The lesser spatial orbital extension expected from Fe^{2+} and Fe^{3+}, relatively weakly bonded at the nitrogen end of the CN^- presumably allows only feeble additional mixed-valence interaction between these centres and so little or negligible stabilisation to intermediate compositions in the PB → PW range. The problem of accommodating extra cations within the lattice over this range may also be relevant. The effect on the c.t. spectra of such additional delocalisation in the oxidised range is not simply predicted, and the *ca.* 12% observed lowering in the energy of the c.t. maximum on going to only traces of $Fe^{II}(CN)_6$ is not ascribable to a single obvious interaction.

The integral stoicheiometries, observed for the PB → PW transformation, contrast with the oxidation observations in a manner consistent with the relative sharpnesses observed for the respective voltammetric peaks (Figure 9B of ref. 7): the peaks on Pt for PW formation and re-oxidation are far sharper than those involving PY formation and reversion in accord with the participation of only two definite species in the former but a range of species in the latter. (The potential needed for total oxidation is more positive on conducting glass than on Pt,[7] 1.20 *cf.* 1.00 V, and the peak for PW formation is also broadened; the changes are in line with expectation for an n-doped semiconductor substrate.)

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