the National Institutes of Health (Grant GM 38401), and NATO (Grant 0034/85). We thank Professor D. N. Hendrickson (University of Illinois) for the computer simulation of the magnetic susceptibility data, Professor W. Haase and Dr. H. Astheimer (Institut für Physikalische Chemie, THD) for the magnetic susceptibility measurements, and Erik Shankland (University of Washington) for running some of the NMR spectra.

Supplementary Material Available: Listing of the anisotropic thermal parameters (1 page); tables of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

Contribution from the Kenan Laboratories of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Observations on the Composition of Prussian Blue Films and Their Electrochemistry

C. A. Lundgren and Royce W. Murray*

Received September 1, 1987

Cyclic voltammetric, energy dispersive X-ray analysis, XPS, ferric equivalent weight, and spectroelectrochemical observations have been made of Prussian blue films grown on Pt and SnO_2 electrodes, aiming at an improved picture of the composition and electrochemical reactions of the ferric ferrocyanide films. EDX shows that as-grown films contain no alkali-metal cation and a chloride impurity, similar to results reported for the single-crystal insoluble form Prussian blue by Ludi et al. The film's composition is altered, however, to an alkali-metal content intermediate between those of insoluble and soluble form Prussian blue, upon cyclical electrochemical reduction of the film's ferric states. Ferric sites are lost, and some alkali-metal cation is incorporated into the film. A compositional model is drawn on the basis of analytical and ferric equivalent weight results. Behavior of the films during voltammetric oxidation is consistent with the model, and no electrolyte anion dependencies on the redox potentials are found. Two different kinds of ferric sites are expected on the basis of the observation that the film has a partly insoluble form composition. These two sites are detected in three ways, by splitting of the voltammetric peak in K^+ and NH_4^+ electrolytes, by spectral observation in KCl that two absorbance changes occur that correlate with the potentials of voltammetric peaks, and by previous observations by Feldman and Murray that the films in alkali-metal and ammonium electrolytes exhibit two ferric states with differing electron self-exchange rates as well as differing potentials in alkali-metal and ammonium electrolytes.

Interest in ferric ferrocyanide (Prussian blue, Fe(III/II)), an important member of the family of metal hexacyanometalates,[1] was renewed several years ago by the development of procedures[2,3] for coating it as films on electrodes. Electrochemical reactions of the mixed-valent coatings gave new insights into Prussian blue electron-transfer chemistry[4] and spectroscopy.[5] This research and analogous cyanometalate work by Bocarsly et al.[6] and Crumbliss et al.[7] has recently been reviewed.[8]

Prussian blue has been described in two formulations, the "soluble" form, $\mathrm{KFe^{III}[Fe^{II}(CN)_6]}$, and the "insoluble" form, $\mathrm{Fe^{III}_4[Fe^{II}(CN)_6]_3{\cdot}6H_2O}$, with the common names having historical peptization rather than actual solubility connotations. Keggin and Miles[9] suggested for the soluble form a face-centered cubic lattice structure in which the high-spin ferric and low-spin ferrocyanide sites are each octahedrally surrounded by -NC and -CN units, respectively, with the K^+ counterion being in an interstitial site. The insoluble Prussian blue structure described in the single crystal study by Ludi et al.[10,11] is also a (primitive) cubic lattice, but one-fourth of the $\mathrm{Fe^{II}(CN)_6}$ units are missing, with their nitrogen sites occupied instead by water molecules coordinated to Fe(III) sites and with as many as eight additional water molecules located interstitially.

It has turned out that uncertainties about which of these two stoichiometries of Prussian blue films (if either) represent the films on electrodes have hampered interpretation of the electrochemical studies.[8] The ferric/ferrous reduction reaction for Prussian blue coatings is written by Neff et al.[12] as of the soluble form

$$\mathrm{KFe^{III}[Fe^{II}(CN)_6] + e^- + K^+ \rightarrow K_2Fe^{II}[Fe^{II}(CN)_6]} \tag{1}$$

and by Itaya et al.[5] as of the insoluble form

$$\mathrm{Fe^{III}_4[Fe^{II}(CN)_6]_3{\cdot}6H_2O + 4e^- + 4K^+ \rightarrow K_4Fe^{II}_4[Fe^{II}(CN)_6]_3{\cdot}6H_2O} \tag{2}$$

Both reduction reactions require, for electroneutrality, entry of K^+ (or another appropriately sized electrolyte cation) into the lattice, and experimental results confirm such a cation dependency.[5,12,13]

The ferrocyanide/ferricyanide oxidation reactions are also written differently, as[12]

$$\mathrm{3KFe^{III}[Fe^{II}(CN)_6] - 2e^- - 2K^+ \rightarrow KFe^{III}_3[Fe^{III}(CN)_6]_2[Fe^{II}(CN)_6]} \tag{3}$$

where part of the lattice K^+ departs from the lattice and the oxidative charge is two-thirds of the reductive charge, and as[5]

$$\mathrm{Fe^{III}_4[Fe^{II}(CN)_6]_3{\cdot}6H_2O - 3e^- + 3X^- \rightarrow Fe^{III}_4[Fe^{II}(CN)_6]_3(X)_3{\cdot}6H_2O} \tag{4}$$

where an electrolyte anion enters the lattice and the oxidative charge is three-fourths of the reductive charge. The reported[5] charge ratio, 0.71, is an indecisively intermediate value. Analyses by Itaya et al.[5] show as-grown Prussian blue films contain no K^+, which is inconsistent with the soluble formulation, but on the other hand, the soluble formulation of reaction 3 is favored by shifts of the potentials of the electrochemical waves with electrolyte concentration,[12] mass *loss* data,[13] and comparative insensitivity to electrolyte anion identity.[12,13]

We originally became interested in using Prussian blue in a bilayer electrode[14] and as an object of a electron-hopping kinetics study,[15] since it is an ostensibly internally ordered electroactive material. In view of the previous uncertainties about the composition of the electrode coatings, we mounted the analytical,

---

(1) Sharp, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; Academic: London, 1976; pp 121-126.
(2) Neff, V. K. *J. Electrochem. Soc.* **1978**, *125*, 886.
(3) Itaya, K.; Akahoshi, H.; Toshima, S. *J. Electrochem. Soc.* **1982**, *129*, 1498.
(4) Rajan, K.; Neff, V. D. *J. Phys. Chem.* **1982**, *86*, 4361.
(5) Itaya, K.; Ataka, T.; Toshima, S. *J. Am. Chem. Soc.* **1982**, *104*, 4767.
(6) Sinha, S.; Humphrey, B. D.; Bocarsly, A. B. *Inorg. Chem.* **1984**, *23*, 203.
(7) Crumbliss, A. L.; Lugg, P. S.; Morosoff, N. *Inorg. Chem.* **1984**, *23*, 4701.
(8) Itaya, K.; Uchida, I.; Neff, V. D. *Acc. Chem. Res.* **1986**, *19*, 162.
(9) Keggin, J. F.; Miles, F. D. *Nature (London)* **1936**, *137*, 577.
(10) Buser, H. J.; Schwarzenbach, D.; Petter, W.; Ludi, A. *Inorg. Chem.* **1977**, *16*, 2704.
(11) Herren, F.; Fischer, P.; Ludi, A.; Halg, W. *Inorg. Chem.* **1980**, *19*, 956.
(12) Ellis, D.; Eckhoff, M.; Neff, V. D. *J. Phys. Chem.* **1981**, *85*, 1225.
(13) Feldman, B. J.; Melroy, O. R., submitted for publication in *J. Electroanal. Chem.* Interfacial Electrochem.
(14) Abruna, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1.
(15) Feldman, B. J.; Murray, R. W. *Inorg. Chem.* **1987**, *26*, 1702.

0020-1669/88/1327-0933$01.50/0

electrochemical, and spectroscopic study described here in support of our bilayer and electron-transport objectives. The results help to clarify existing problems of film composition, spectroscopy, and electron-transfer chemistry and support our published observation[15] that Prussian blue films contain *two* ferric/ferrous couples, with discernibly different formal potentials and with electron self-exchange (hopping) rates that differ by about 10×. We proposed that the faster electron-conducting ferric/ferrous couple might be the symmetrically –NC coordinated sites. The results presented here show that electrochemically grown and reductively cycled Prussian blue films have a composition intermediate between the soluble and insoluble formulas and that the two electrochemically distinguishable ferric sites are also spectroscopically distinguishable.

Experimental Section

Chemicals. Reagent grade chemicals were used as received. Solutions were prepared with triply distilled water.

Electrode Coating. Teflon-shrouded Pt electrode disks (ca. 0.15 cm^2) were cleaned in concentrated HCl and polished with 1-μm diamond paste prior to each use. Prussian blue films were grown both by dip coating[2] and by a potentiostatic procedure we have used before.[15,16] (The previous electrochemical procedure used constant current for film growth and entailed a considerable, gradual change in electrode potential during film growth;[5] this could produce undesirable chemical heterogeneity in the film.) Dip coating involved potentiostating the clean electrode in 0.1 M HCl at –0.55 V vs SSCE for 90 s, vigorously evolving H_2, rinsing with distilled water, and immediately exposing the electrode to a solution containing 2 mM $FeCl_3$, 2 mM $K_3Fe(CN)_6$, 0.01 M KCl, and 0.01 M HCl for from 1 to 3 h.

Films were electrochemically grown by potentiostating a clean electrode at 0.51 V vs SSCE for typically 3 min in the same growth solution as above. This potential ensures that as-grown films are initially in the Fe(III/II) state. All electrodes were washed with distilled water for 5 min after growth, rinsed in acetone, and dried in a desiccator overnight. Except as noted, all data reported are for potentiostatically grown films.

Electrochemical experiments were conducted in conventional divided compartment cells with Pt-wire auxiliary and NaCl–saturated calomel reference electrodes (SSCE). For spectroelectrochemical experiments, the films were grown potentiostatically as above but on optically transparent SnO_2 film electrodes.[17] Transmission spectra were taken by using a two-compartment cell with Pyrex optical flat windows and a Tracor Northern TN-1710 UV-VIS diode array spectrometer, at 25–100 mV intervals while slowly scanning (2 mV/s) the SnO_2 potential.

Prussian blue films grown on 2.5 cm^2 Pt foils were weighed with a Cahn microbalance following at least 17 h of drying in a desiccator. The net weight of the film relative to the charge required to reduce the ferric iron gave an equivalent weight (g/mol of electron) for ferric reduction.

Energy dispersive X-ray analysis (EDX) was performed on an International Scientific Instruments DS-130 SEM with a Tracor Northern TN-5500 energy dispersive X-ray analyzer.

Results and Discussion

Voltammetry. Typical cyclic voltammetry (Figure 1) in 0.5 M KCl of a Prussian blue film potentiostatically grown on a Pt electrode is similar to that reported previously and is shown here for reference. It exhibits two main features.

A negative potential scan causes reduction of the mixed-valent ferric ferrocyanide form, Fe(III/II), to Fe(II/II), Prussian white (colorless), in a multifeatured wave consisting of a sharp feature centered (average of $E_{p,c}$ and $E_{p,a}$) at 0.19 V vs SSCE and another broader shoulder at a more negative potential of ca. 0.14 V, comprising a fraction of the overall charge. Another small shoulder is often seen[16] on the positive side of the wave, at 0.3 V vs SSCE, on the first reductive scan, but is greatly diminished thereafter and is not noticeable in Figure 1. These details are preserved, with slight variations, in voltammograms in KCl, KNO_3, K(Tos) and KPF_6 electrolytes.

It is significant that the 0.14 V shoulder during ferric reduction appears consistently (albeit with varying definition) in published Prussian blue voltammograms in potassium electrolytes irrespective of the film growth technique or electrode material (SnO_2,[3,5,8,18] Au,[8,12,13] glassy carbon,[19] and Pt[16]). The broad wave at 0.14 V is not specious proton reduction because it appears with electrode materials like SnO_2 and carbon; it is enhanced by having excess ferric iron present in the growth medium,[12] and also appears in ferric hexacyanoosmium voltammetry.[8] An analogous shoulder appears with Prussian blue films in NH_4^+ electrolyte (Figure 2), where the central wave is sharp (vide infra) like that in K^+ electrolyte, but (at 50 mV/s) not in other electrolytes (Figure 2) because there the central waves are broad and obscure it. However, at very slow potential sweep rates (Figure 3), the shoulder on the negative side of the most prominent wave can be seen in Rb^+ and Cs^+ as well as in K^+ and NH_4^+ electrolytes. Estimated potentials for the main and shoulder waves ($E^{\circ\prime}$ and $E_{sh}^{\circ\prime}$ are given in Table I. Although the shoulder at $E_{sh}^{\circ\prime}$ is small, we attach importance to the ferric state that it represents because we have found that as a redox couple it exhibits an electron conductivity (electron self-exchange rate constant) about 10× larger than that of the more prominent sharp wave in the various electrolytes.[15] We will spectrally confirm the existence of two chemical states of ferric iron later, and regard these states as important to a full interpretation of Prussian blue electrochemistry.

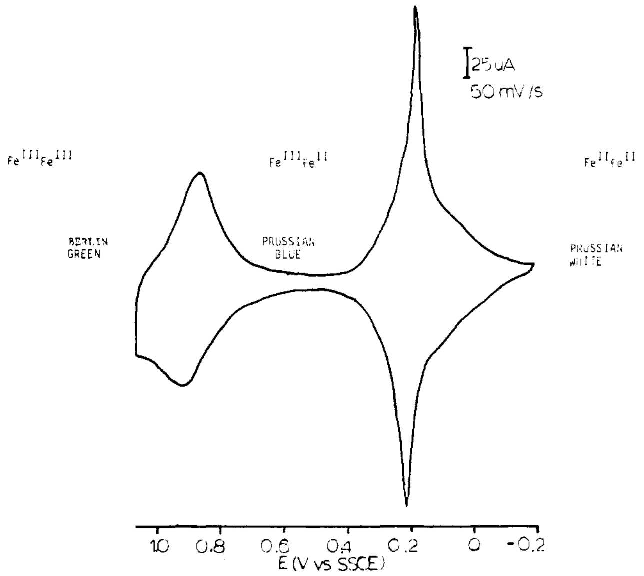

Figure 1. Cyclic voltammogram of PB-coated (PB = Prussian blue) Pt electrode in 0.5 M KCl.

The oxidation of Prussian blue in a positive potential scan in KCl electrolyte (Figure 1) corresponds to partial or full oxidation of the ferrocyanide sites to Berlin green or Prussian yellow, depending on the positive extent of the potential scan.[5] The charge under the oxidation waves in Figure 1 is 73% of that in the reduction wave on Pt. The oxidation voltammograms in KCl, KNO_3, and K(Tos) were virtually identical, and they (and those in NaCl), were fairly stable *provided* the film had been *previously* cyclically reduced in that electrolyte; otherwise, a considerable loss of charge occurred in successive scans. The potentials for the oxidation waves are given in Table I for varying cations; there are small variation among the cations as seen, but we observed no significant variation among anions (i.e., KCl, KNO_3, K(Tos)).

Figures 2 and 3 compare voltammetry for ferric reduction in different alkali-metal cation and NH_4^+ salt solutions. These patterns were quite similar whether the film had been grown potentiostatically or by the dip method, and in the case of the KCl and NaCl electrolytes, the results were the same whether the growth solution was composed of K^+ or Na^+ salts. It is already known[5-7] that metallocyanate films exhibit electrolyte cation-dependent formal potentials and voltammetric shapes; we use these data to point out certain additional features. The virgin and the subsequent voltammetric scans (Figure 3) are somewhat different, with a greater charge for ferric reduction seen in the first scan;

---

(16) Chidsey, C. E.; Feldman, B. J.; Lundgren, C.; Murray, R. W. *Anal. Chem.* **1986**, *58*, 601.

(17) Kuwana, T.; Heineman, W. *Acc. Chem. Res.* **1976**, *9*, 241.

(18) Itaya, K.; Uchida, I. *Inorg. Chem.* **1986**, *25*, 389.

(19) Itaya, K.; Shoji, N.; Uchida, I. *J. Am. Chem. Soc.* **1984**, *106*, 3423.

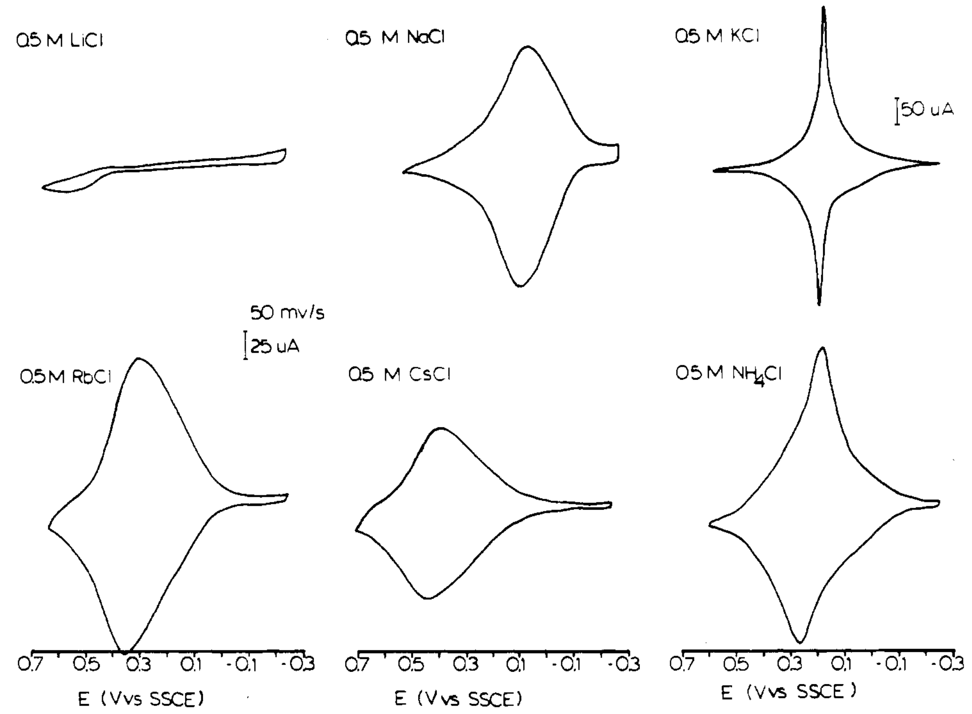

Figure 2. Cyclic voltammograms of PB films on Pt electrodes in various cation electrolytes. Scan speed = 50 mV/s; $A = 0.15$ cm^2.

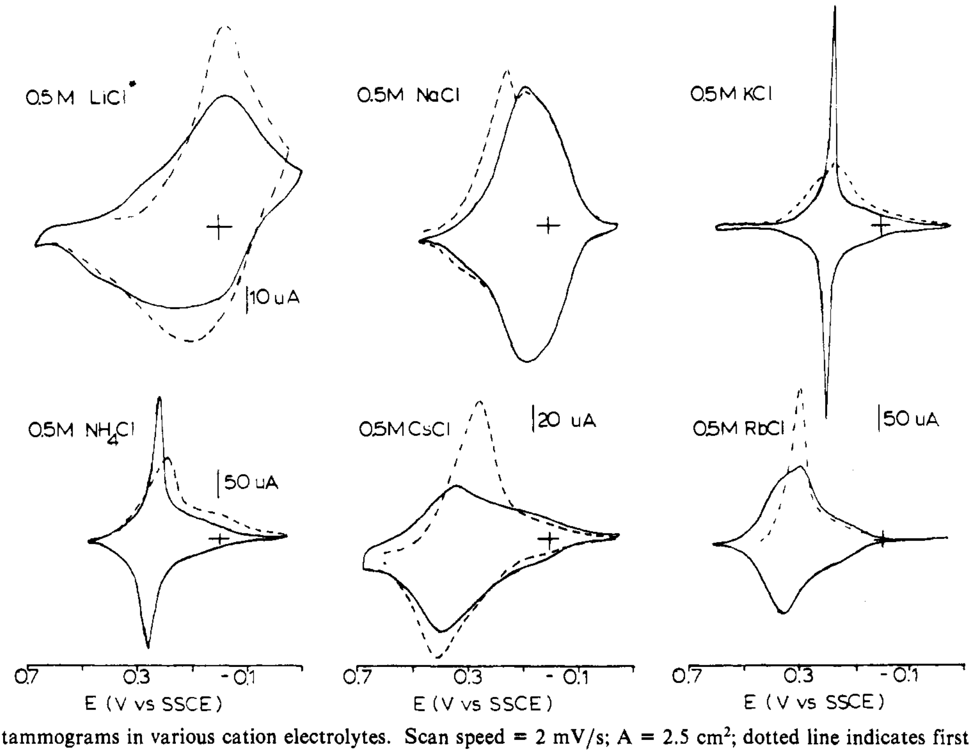

Figure 3. Cyclic voltammograms in various cation electrolytes. Scan speed = 2 mV/s; A = 2.5 cm^2; dotted line indicates first reduction; solid line indicates second reduction. Cyclic voltammogram in 0.5 M LiCl obtained by previously reducing the PB in 0.5 M KCl.

we will use this charge data in the following section. The voltammograms are stable after the initial scan, except for those in LiCl and CsCl, which slowly decay upon repeated scanning. Contrary to a previous report,[5] voltammetry in NaCl is stable irrespective of previous drying of the as-grown film. (We found that, in general, prior desiccator drying substantially enhanced the stability of the observed voltammetry.) While voltammetry in LiCl electrolyte has been reported,[7,20,21] we were only able to observe a somewhat unstable wave in LiCl by first cyclically reducing the ferric states in KCl (otherwise no reduction was seen at all). The voltammetry thus obtained in LiCl may be affected by K^+ ions retained in the film, but the substantial shift in the potential of the wave (as compared to that in KCl) makes it clear that Li^+ ions are also inserted into the film. No voltammetry was seen in Et_4N^+ electrolyte under any circumstances.

Table I lists the formal potentials ($E°'$) for the most prominent current peak and the shoulder ($E_{sh}°'$) observed (Figure 2) in each electrolyte. Table I also lists the half-wave potential ($E_{1/2}$) measured elsewhere[15] for the faster of the two different electron-conducting ferric redox couples in these films. $E_{sh}°'$ and $E_{1/2}$ differ slightly probably because of uncertainty in the shoulder wave potentials; both values definitely differ from $E°'$ in each electrolyte.

---

(20) Crumbliss, A. L.; Lugg, P. S.; Childers, J. W.; Palmer, R. A. *J. Phys. Chem.* **1985**, *89*, 482.

(21) Messina, R.; Perichon, J. *J. Appl. Electrochem.* **1980**, *10*, 655.

Table I. Potentials for Prussian Blue Film Reduction (Ferric Sites) and Oxidation (Ferrocyanide Sites)

	redn					oxidn	
electrolyte	$E^{\circ\prime}$,[a] V	$E_{sh}{}^{\circ\prime}$,[b]	$E_{1/2}$,[c] V	ionic radius, Å	E_{hyd},[d] V	E_{pa},[e]	E_{pc},[e] V
LiCl	−0.04[g]		NA	0.6	5.07	NA	NA
NaCl	0.08		0.049	0.95	4.08	1.01	1.00, 0.82
KCl	0.187	0.11	0.014	1.33	3.34	0.89	0.84
NH_4Cl	0.22	0.12	0.17	0.99	0.82		
RbCl	0.34	0.19	0.26	1.48	3.17	1.04[g]	0.99, 0.88[g]
CsCl	0.41	0.18	0.33	1.69	2.45	1.10[g]	0.85[g]

[a] Average of reduction (E_{pc}) and oxidation (E_{pa}) peak potentials of the most prominent wave in ferric reduction voltammograms like Figures 1–3. (vs SSCE). [b] Average of reduction (E_{pc}) and oxidation (E_{pa}) peak potentials of the shoulder on the negative potential side of the most prominent wave as from ferric reduction voltammograms like Figure 3 scanned at 2 mV/s (vs SSCE). [c] Half-wave potential for redox of the faster of the two observed electron conducting ferric states (vs SSCE).[15] [d] E_{hyd} values calculated from free energy of hydration values. [e] Observed ferrocyanide oxidation (E_{pa}) and rereduction (E_{pc}) peak potentials (vs SSCE) were not averaged to give a formal potential because in the case of Na^+ and Rb^+ the rereduction wave is split. [f] $E^{\circ\prime}$ in LiCl obtained by first reducing the film in KCl. [g] $RbNO_3$ and $CsNO_3$ used rather than the chloride salts.

Table II. EDX Analysis of Prussian Blue Films on Pt

		atom %[a]				
		Fe	Cl	K	Fe:Cl	Fe:K
as-grown		87.5	11.5	1.0		
		90.4	9.6	0		
	av	90.0	10.5	0.5	9	...
immersed in 0.5 M KCl at 0.3 V		89.2	5.7	5.0		
		84.5	8.7	6.8		
	av	86.8	7.2 ± 1.5	5.9 ± 0.9	12	14
cyclically reduced (3 scans) to Fe(II/II) in 0.5 M KCl		76.9	12.7	10.4		
		82.0	6.0	12.0		
		83.5	8.6	7.9		
		81.2	6.4	12.3		
		75.3	8.8	15.9		
		74.4	9.4	16.2		
	av	78.9	8.7 ± 1.6	12.4 ± 2.4	9	6.4
oxidized at 1.0 V in 0.5 M KCl		99.2	0.8	0		
		98.8	1.2	0		
	av	99.0	1.0	0	99	...
oxidized at 1.0 V and rereduced to Fe(III/II) in 0.5 M KCl		84.9	4.1	11.0		
		79.1	6.1	14.8		
	av	82.0	5.1 ± 1	12.9 ± 1.9	16	6.4

[a] Only elements detectable; C and N do not appear by EDX.

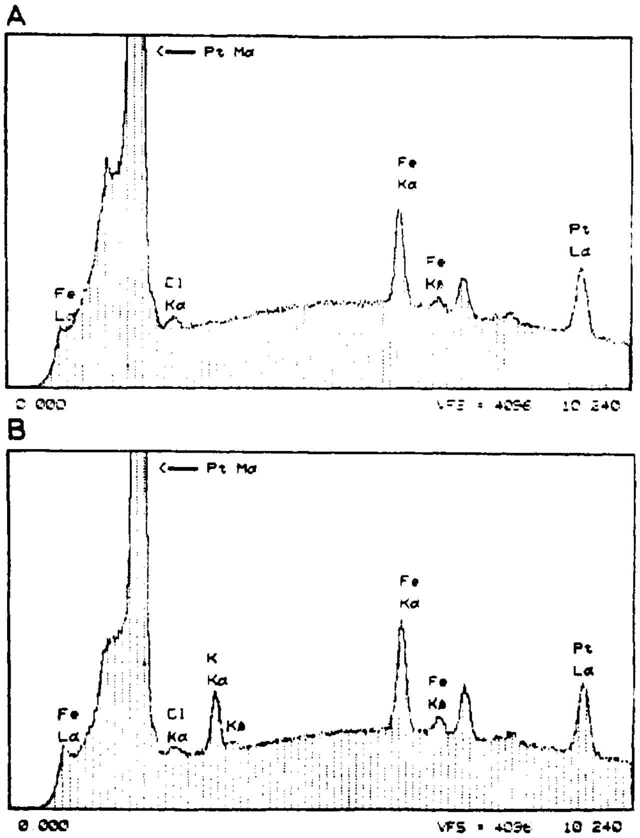

Figure 4. EDX spectra of PB-coated Pt electrodes: (A) PB film as grown; (B) PB film reduced in 0.5 M KCl three times. Accelerating voltage = 10 kV.

That is, the films consistently in all electrolytes display two electroactive ferric states, the one with the more positive potential (i.e., 0.19 V in KCl) being present in greater quantity and the lesser one, with the more negative potential (i.e., 0.14 V in KCl), becoming evident through a much faster site-site electron hopping rate. Spectral data that also support the second ferric state are given later.

The potential of the reduction wave is known to vary with cation by several hundred millivolts. This phenomenon is also evident in other cyanometalates; Bocarsly has noted a linear relationship between reduction potential and ionic radius of the alkali cation.[6] The reduction potentials $E^{\circ\prime}$ in Table I also vary linearly with ionic radius. An explanation for the systematic potential change has not been offered. It is possible that these cations do not retain a complete hydration shell upon entrance to the crystal lattice. The hydration energies in volts, calculated from free energy of hydration values, are given (E_{hyd}) for each of the alkali cations in Table I. The E_{hyd} values vary by as much as 2.5 V between Cs^+ and Li^+, an energy much larger than the observed $E^{\circ\prime}$ shift. From the magnitude of the difference between the E_{hyd} values it can be inferred that even a partial dehydration of the cations, in order for them to be of the appropriate size to enter the crystal lattice, can require enough energy to explain the smaller differences in $E^{\circ\prime}$ reduction potentials observed.

Analytical Studies and Compositional Model. As noted above, a major problem in understanding Prussian blue film electrochemistry is its uncertain composition. In particular the K^+ content of the films should reflect which form, soluble or insoluble, of the mixed-valent compound is present. A series of films was analyzed by EDX to explore this problem, with results shown in Table II. The EDX (and some XPS) measurements on potentiostatically grown films (on Pt) reveal *no* K^+ in the as-grown films. However Cl^- was consistently found in a Fe:Cl atom ratio of 9:1 (Figure 4A and Table II). Furthermore, the composition of the films changes somewhat according to subsequent treatment. K^+ appears in the film (atom ratio Fe:K = 14.1) as a result of simply immersing an as-grown film in 0.5 M KCl (at open circuit); the Cl^- content of the film concurrently decreases somewhat, to about the same atom ratio to Fe as the Fe:K ratio. Additional K^+ is incorporated into the film (atom ratio Fe:K decreases to 6.4:1) as a result of cyclically reducing and reoxidizing the ferric states by potential scanning through the Fe(III/II),Fe(II/II) wave in a (pH 4) 0.5 M KCl solution (Figure 4B). (A similar Fe/Cs ratio was obtained if the cyclical reduction was done in CsCl solution, so the effect is not peculiar to the K^+ electrolyte.) The Fe/Cl content is not changed by cyclical reduction through the Fe(II/II) state, even if conducted in 0.5 M KNO_3 rather than KCl. As for oxidations of the ferrocyanide states, using a film in which the ferric states had been previously reductively cycled, oxidation of the ferrocyanide sites at 1.0 V vs SSCE in KCl

Table III. Equivalent Weights for Prussian Blue Films[a] for Ferric Reduction

					ferric equiv wt, g/mol				% mass change after 2 cyclical redns			
							calcd[d]			calcd[d]		
electrolyte cation[b]	Q_{growth},[c] C/cm^2	Q_1, C/cm^2	Q_2, C/cm^2	Q_2:Q_1	1st scan (equiv wt$_1$)	2nd scan (equiv wt$_2$)	case A	case B	exptl	case A	case B	ferric:ferrocyanide ratio[d] after cyclical redn
NH_4^+	0.0131	0.0163	0.0137	0.84 + 0.03	266 ± 13	202 ± 20	254	228	−24	+1.5	−9	3.36:3
Na^+	0.0149	0.0158	0.0137	0.84 ± 0.03	269 ± 49	256 ± 50	258	230	−14	+3	−7	3.39:3
K^+	0.0147	0.0149	0.0138	0.98 ± 0.02	245 ± 28	278 ± 23	264	247	−1.4	+6	−1	3.92:3
Rb^+	0.0150	0.0195	0.0163	0.84 ± 0.02	266 ± 88	322 ± 72	303	245	+10	+21	−2	3.34:3
Cs^+	0.0145	0.0120	0.0101	0.84 ± 0.01	398 ± 6	602 ± 68	337	257	+21	+34	+3	3.37:3

[a] Grown potentiostatically as described in the Experimental Section. [b] 0.5 *M* C^+Cl^- electrolyte salt in which film is subsequently reduced to Fe(II/II) and reoxidized, twice, giving charges Q_1 and Q_2 for virgininal and second reduction. [c] Charge consumed to grow the film minus charging current. [d] See text.

drastically decreases the Cl^- content and drives all of the K^+ from the film. Rereduction back to the Fe(III/II) state reproduces the same K^+ and Cl^- content as found after cyclical reduction.

The incorporation of K^+ into the Prussian blue lattice by simple immersion in KCl is accountable for by an exchange of K^+ for some ion resident in the film after growth. This ion exchange and the presence of a similar Fe/Cl ratio for impurity Cl^- were earlier noted by Ludi et al.[10] in *single-crystal insoluble form* Prussian blue; this was apparently overlooked by recent workers.[8] Neff et al.[12] assumed that film growth in solutions containing excess K^+ would produce the K^+-containing soluble form of Prussian blue, whereas Itaya et al.[5] by spectroscopic analysis could detect no K^+ in as-grown films that had been prepared in the absence of excess K^+. We agree with Itaya et al.[5] that no K^+ is present in as-grown Prussian Blue films, even though excess KCl was present in the (acidic) growth solution, but find on the other hand that K^+ can enter the lattice subsequently by simple ion exchange in a KCl solution of higher pH.

These results clarify some points about the composition of (potentiostatically) *as-grown* Prussian blue films. The K^+ content is consistent with the insoluble, not the ideal soluble, form of Prussian blue; the latter should contain an Fe:K atom ratio of 2:1, whereas as-grown films contain no K^+. Second, the presence of the Cl^- impurity requires an additional cationic charge. Third, the reason K^+ enters the lattice upon immersion in 0.1 M KCl but not during film growth in the presence of 0.01 M KCl can be accounted for both in terms of the differing KCl concentrations and (probably more importantly) the higher pH of the immersion solution (pH 4). Fourth, the persistence of the Cl^- impurity (even upon film reduction in KNO_3) suggests that it is a strongly coordinated and not an interstitial species. Finally, the coordinated Cl^- and the immersion-incorporated K^+ are present in similar quantities, one per 12 Fe and one per 14 Fe, respectively.

These points lead us to propose, as did Ludi et al.,[10] that the *as-grown films* have a Cl^--contaminated insoluble form structure. The Cl^- impurity is ferric coordinated, and its charge in the as-grown films is compensated by protons either as interstitial H_3O^+ or more plausibly as ferric-bound hydronium. In the higher pH immersion solution, the proton exchanges with K^+ (or whichever alkali-metal cation is present), which enters the lattice as the counterion to the Cl^- impurity. In the ideal insoluble form, one-fourth of the ferric sites would have six isocyano ligands and three-fourths of the ferric sites would have four isocyano and two water ligands.[10] In the Cl^--contaminated insoluble form, one water on about a third of the former sites may be replaced with chloride. Ludi et al.[10] suggest in fact that the Cl^- impurity may play a role in the nonstatistical distribution of ferrocyanide vacancies (i.e., lattice sites where the ferric moiety is coordinated by something other than −NC) in single-crystal insoluble Prussian blue.

Proceeding to the composition of films that have been electrochemically reduced or oxidized, we next present weighing experiments that measure the ferric equivalent weight for electrochemical reduction of films from Fe(III/II) to Fe(II/II). Table III lists the charges (Q_{growth}) for potentiostatically depositing a series of films that were then thoroughly washed, dried in a desiccator, weighed (typical 30–50 μg), twice cyclically reduced to measure the charges Q_1 and Q_2 needed to reduce them for the initial and second times to the Fe(II/II) stage in the electrolyte solutions indicated in Table III, washed and redried, and reweighed. The two charges and initial and final weights give the ferric equivalent weights equiv wt$_1$ and equiv wt$_2$ shown in Table III.

Table III reveals that in all electrolytes (but marginally in K^+) the charge Q_1 for the reduction of a virgin as-grown film exceeds that (Q_2) of subsequent reductions (which are generally thereafter fairly stable except for reduction of Cs^+, which continues to change). The *ratio* of the two charges, Q_2:Q_1, is nearly the same for all the cations. Mass changes, both decreases and increases, also occur in the films in the percentage indicated; the order of percentage mass change falls exactly in the order of the electrolyte cation masses. These systematic effects suggest that a chemical change occurs upon cyclical reduction of the film that is common to all the electrolytes.

The chemical change is (at least in part) associated with a loss of ferric iron from the film. Solubilized ferric iron could be detected in the electrolyte solution following cyclical reduction of a thick Prussian blue film on a large electrode contacted by a small volume of KCl solution. After removal of the electrode, 2,2′-bipyridine was added to the solution, which with warming displayed the pink color characteristic of the $Fe(bpy)_3^{3+}$ complex in the solution. Repeating this experiment in a NaCl solution gives an even more intense coloration, so the ferric expulsion seems general. No ferric loss occurs simply upon immersion; cyclical reduction is required.

The above data show that, upon cyclical reduction of insoluble form Prussian blue, additional K^+ is incorporated (Table II), some ferric ion is lost (Table III), and mass changes occur that are systematic with the nature of the electrolyte cation (Table III). Mortimer and Rosseinsky[22] have proposed that reductive cycling of Prussian blue films in K^+ electrolyte causes an irreversible change from an as-grown insoluble form to the soluble form. Their model is assumed in the microbalance study by Feldman and Melroy.[13] Our data support such a change but show that it is not quantitative. The film after reductive cycling has a composition intermediate between the insoluble and soluble forms, meaning that some but not all lattice sites continue to have ferrocyanide vacancies. Significantly, except for K^+, the intermediate composition seems not to depend greatly on the particular electrolyte cation involved. Also, an important feature of the analytical results is that the retention of excess ferric sites in the Prussian blue lattice is consistent with the electrochemical observations noted above in connection with Table I and with the spectroelectrochemical results presented later, showing that the films contain two different kinds of ferric sites.

It seems worthwhile at this point to attempt an exercise of formulating a compositional model that reproduces the order and quantity of mass changes and equivalent weights in Table III. Some assumptions will be necessary. The results for as-grown films have suggested an insoluble form composition with a Cl^- impurity charge compensated with a K^+-exchangeable proton, i.e., $(HCl)Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot 6H_2O$, assuming that our desiccator

---

[22] Mortimer, R. J.; Rosseinsky, D. R. *J. Chem. Soc., Dalton Trans.* **1984**, 2059.

drying removes interstitial but not bound waters. The ferric:ferrocyanide ratio in the as-grown film is taken as 4:3. If we interpret the charge ratio $Q_2:Q_1$ as equal to the fractional change $1 - Z/4$ in the lattice ferric iron caused by cyclical reduction in the various electrolytes, the ferric:ferrocyanide ratio that exists in the modified film is given in the right-hand column of Table III. We assume that the lost ferric charges are compensated by insertion of $3Z$ electrolyte cations into the Fe(III/II) lattice. Extension of the model beyond this point must cope with the fact that our analytical data are for K^+ and Cs^+ only and do not include the film water content, so assumptions are made that produce two extremes within the framework of the analytical results. In case A, we assume that the $3Z$ cations are all those of the electrolyte solution used and that water is not lost. In case B, we assume that the electrolyte cation C^+ is incorporated in the atom ratio $Fe:C^+ = 6.4$, just as found for K^+ in Table II, with the remaining cationic charge being protons, and that $6Z$ moles of water are lost. The models correspond (with some rounding off) to the formula

$$(C^+)_{1+3Z}(Cl^-)Fe^{III}_{4-Z}[Fe(CN)_6]_3\cdot(6 - 6Z)H_2O$$

1

where C^+ is entirely alkali-metal cation in case A and is $(H^+)_{3Z}(C^+)$ in Case B.

This model gives the calculated ferric equivalent weight and percentage mass change columns in Table III; they should be compared to the corresponding experimental quantities (exptl % mass change and equiv wt_2). Both models predict the observed trend in equivalent weight and mass change as an increasingly massive cation is exchanged for the ferric moiety. The actual numerical values also agree fairly well with experiment except for the mass loss for NH_4^+ and the equivalent weight for Cs^+ (where instability may be a problem).

The point of the preceding exercise is to show that, with some assumptions, a rational compositional model can be constructed from analytical data that conforms to actual experimental behavior. It accommodates (in case B) the observation of Feldman and Melroy[13] that, in pH 4 K^+ and Rb^+ electrolytes, both protons and alkali-metal cations in roughly equal quantities move into and out of Prussian blue films during their reduction and oxidation. The model emphasizes our belief that the reductively reduced films have a composition intermediate between that of the soluble and insoluble forms; the film has about two-thirds of the difference between ferric and ferrocyanide content eliminated by reduction in all of the cation solutions except K^+ where only a slight ferric loss occurs.

Turning to oxidation of Prussian blue films, Feldman and Melroy[13] observed that mass *loss* occurs during film oxidation to the Fe(III/III) state, and interpreted this as an egress of a combination of alkali-metal cations and protons. That picture is consistent with a lack of dependence of the voltammetry in K^+ electrolyte on the anion used, the small differences in oxidation potentials observed when different cations are used (Table I), the EDX measurements presented in Table II that show K^+ departs the film upon oxidation, and the compositional model **1**. A film oxidized in KCl does not gain Cl^- as would be suggested by reaction 3, but instead *loses* its Cl^- content as well as its K^+. These constituents are restored, nearly quantitatively, to the film upon reduction back to the Fe(III/II) stage. On the basis of this result, oxidation of a film previously reduced in K^+ electrolyte (where $4 - Z < 4$) could be written as

$$(K^+)(Cl^-)Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot 6H_2O - 3e^- \rightarrow Fe^{III}_4[Fe^{III}(CN)_6]_3(OH^-)_3\cdot 3H_2O \quad (5)$$

where because the resident K^+ charge is insufficient to compensate for the ferrocyanide–ferricyanide transformation, additional cationic charges are provided by ionization of ferric-bound water. This equation anticipates that oxidation voltammetry of an as-grown film might differ from that of a previously reduced film; as was mentioned earlier, previously reduced films give stable oxidation voltammetry whereas as-grown films do not.

Spectroelectrochemistry. Visible-range transmission spectra taken of Prussian blue films on SnO_2 electrodes at closely spaced potential intervals in 0.5 M KCl and 0.5 M NaCl are shown in Figures 5 and 6 respectively. As in their voltammograms (Figure

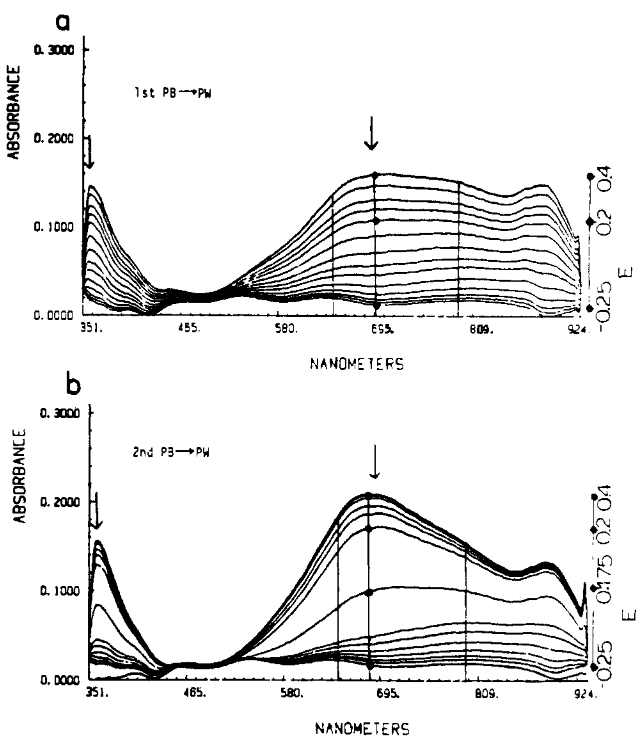

Figure 5. Visible absorbance spectra of PB-coated SnO_2 electrodes in 0.5 M KCl: (A) first reduction of PB to PW; (B) second reduction of PB to PW. Scan speed = 2 mV/s; spectra recorded in 50-mV intervals except in peak center where intervals were 25 mV.

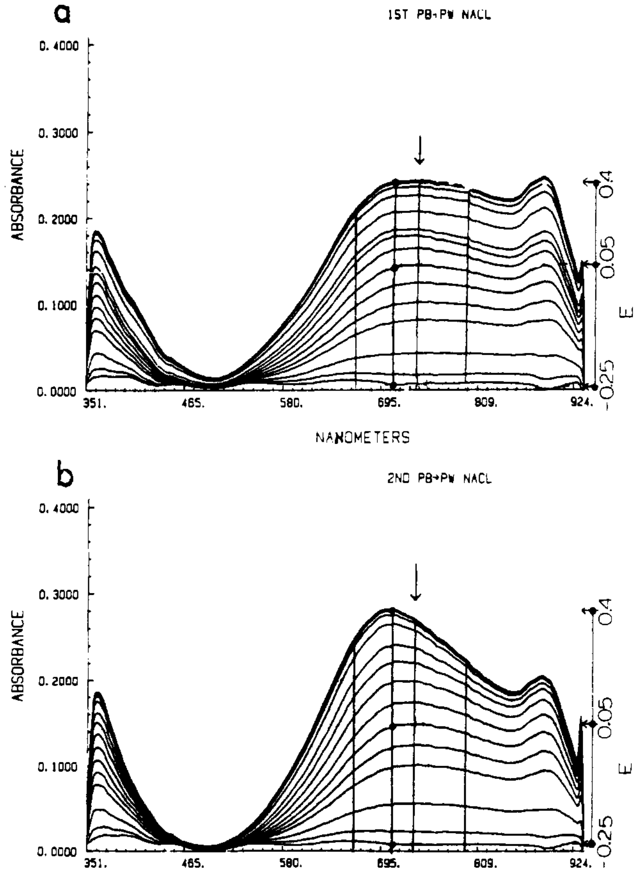

Figure 6. Visible absorbance spectra of PB-coated SnO_2 electrodes in 0.5 M NaCl: (A) first reduction of PB to PW; (B) second reduction of PB to PW. Scan speed = 2 mV/s; spectra recorded in 50-mV intervals except in peak center where intervals were 25 mV.

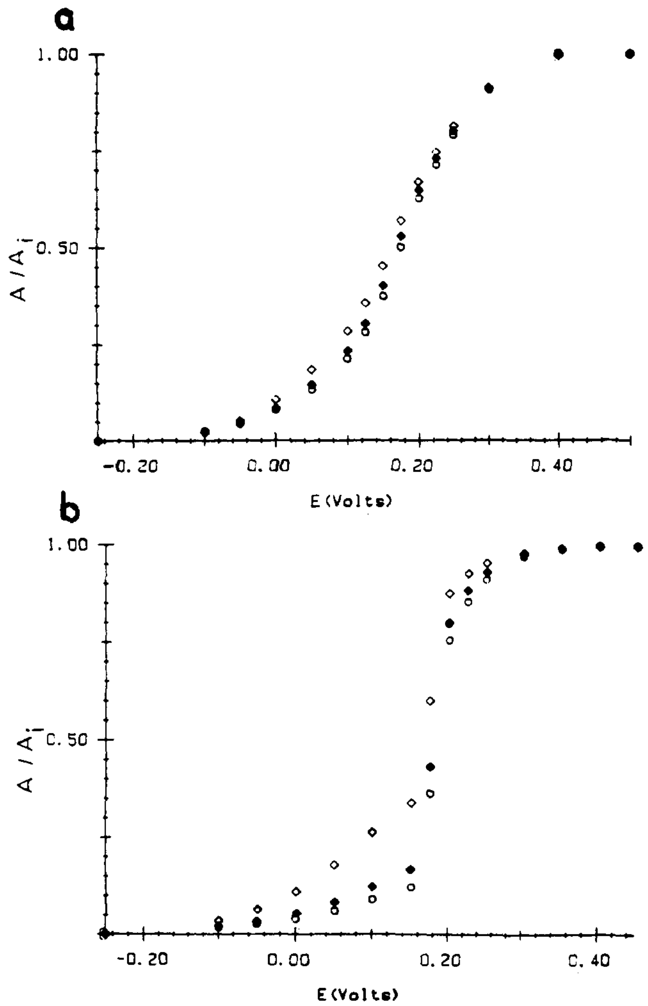

Figure 7. Normalized absorption vs potential in 0.5 M KCl at (◇) 793, (◆) 701, and (○) 645 nm: (A) first reduction of PB; (B) second reduction of PB.

3), spectra of as-grown and of previously reduced films differ, the main effect being higher and lower absorbance in the 701- and 776-nm regions, respectively. Spectra do not change after the initial reduction cycle.

Figure 7 shows how the 645, 701 and 793 nm absorbances change with the applied potential in KCl electrolyte. The absorbances are normalized to the initial highest value for ease of comparison. The initial absorbance–potential response, drawn out (Figure 7A) as is the initial voltammetric scan in Figure 3, is the same at each wavelength. On subsequent scans, however, irrespective of whether potential is varied from positive to negative or *vv*, the absorbances at the two wavelengths change differently with potential (Figure 7B). Those at 645 and 701 nm (○, ◆) undergo a very sharp change centered at 0.19 V vs SSCE; this matches the sharp central peak in the voltammogram in KCl electrolyte (Figure 1). The absorbance at 793 nm (◇) also shows this sharp change but additionally displays a prominent extended tail at a more negative potential which by comparison of Figures 1 and 7B is clearly associated with the 0.14 V vs SSCE shoulder seen in the voltammetry in KCl.

The results of Figure 7 are consistent with the voltammetric and compositional results advanced above, that the Prussian blue films retain part of the insoluble form structure with two different ferric states even after reduction. Following our interpretation[15] of the electron conductivity of the ferric sites that reduce at 0.19 and 0.14 V, we suggest that the absorbances at 645 and 701 nm represent the intervalent charge-transfer transition for the (0.19 V) ferric sites that (in the insoluble formulation) are probably those adjacent to ferrocyanide vacancies and are unsymmetrically coordinated with –NC, water, and possibly impurity Cl^- ligands, whereas that at 793 nm represents the lower energy IVCT transition to (0.14 V) ferric sites that are symmetrically coordinated by –NC groups.

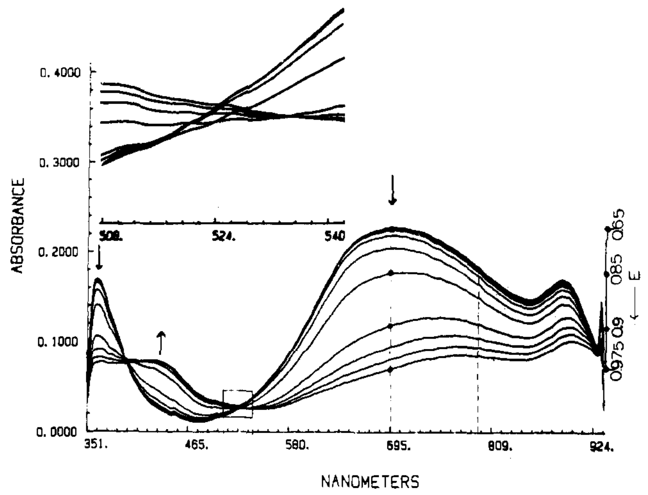

Figure 8. Visible absorption spectra of PB-coated SnO_2 electrodes in 0.5 M KNO_3. Scan speed = 2 mV/s; spectra recorded in 50-mV intervals except in peak intervals were 25 mV.

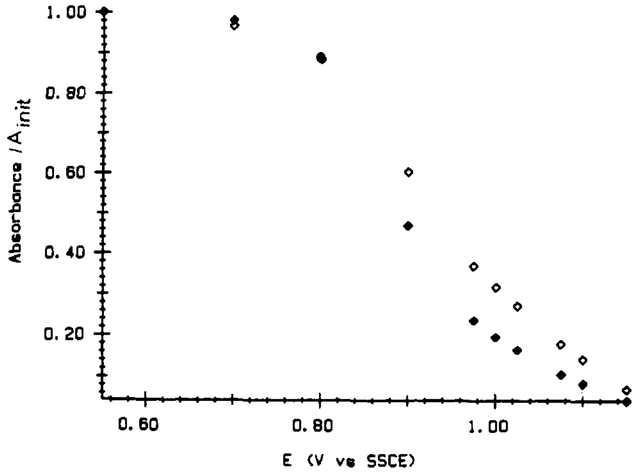

Figure 9. Normalized absorption vs potential in 0.5 M KNO_3 of PB oxidation to BG, at (◇) 793 and (◆) 697 nm.

Spectra like those in Figure 5 were reported previously[18] and were interpreted in terms of an actual shift in the λ_{max} for the Prussian blue intervalent charge-transfer band. Our more detailed potential-dependence data show that this was a misinterpretation, the shift in λ_{max} being only an apparent effect; the absorption spectrum is actually composed of two overlapping ferric components whose reduction and consequent elimination of their IVCT absorbances occur at differing potentials.

As would be expected from there being two different IVCT transitions, the spectroelectrochemical results for oxidation of Prussian blue films in 0.5 M KNO_3 fit a similar pattern, as shown by the spectra in Figure 8 and the plot showing how absorbances at 697 and 793 nm change with the applied potential (Figure 9). Although less distinct than in Figure 6B, the change in absorbance at 697 nm (◆) in Figure 9 is centered at about 0.84 V vs SSCE whereas that at 793 nm (◇) shows an additional change centered at roughly 1.0 V. This smaller feature is not readily resolved in the oxidative voltammetry, but we do see from the Figure 8 inset that two different isosbestic points appearing as the potentials for the oxidation wave are traversed, with the curve at 0.85 V being a transition from one isosbestic to the other.

Acknowledgment. This research was supported by grants from the Office of Naval Research and the National Science Foundation. Assistance from R. Kunz with EDX spectra is gratefully acknowledged.