Electrochemistry of Polynuclear Transition Metal Cyanides: Prussian Blue and Its Analogues

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The study of modified electrode surfaces has had a profound effect on research in the field of electrochemistry in the past decade.[1-4] During this time there has also been a renaissance of interest in the chemistry of the mixed valence compounds.[5] The virtues of the study of mixed valence compounds were originally extolled by Robin and Day in an important review wherein it was pointed out that their chemistry had been neglected.[6] They emphasized the great variety of mixed valence structures and categorized them according to their electronic conductivity and spectral characteristics.

The transition metal hexacyanometallates form an important class of the insoluble mixed valence compounds. They have the general formula $M_k{}^A[M^B(CN)_6]_l$ where M^A and M^B are transition metals with different formal oxidation numbers. They may contain ions other than metals and various amounts of water. Their chemistry has been reviewed extensively.[7-10]

The prototype transition metal hexacyanide is Prussian blue (iron(III) hexacyanoferrate(II)), which is the oldest coordination compound reported in the scientific literature.[11] This highly insoluble polymeric inorganic semiconductor has fascinated chemists since its discovery. Long before modern theories of chemical bonding, its intense blue color, which was known to be uncharacteristic of the solutions of ferric ion and ferrocyanide ion used in its preparation, was ascribed to an "oscillation of valence".[6]

In this account we shall describe recent advances concerning the electrochemistry of electrodes modified by depositing thin films of Prussian blue (PB) or related analogous compounds. Some time ago it was discovered that PB electrodes could be electrochemically oxidized or reduced by a mechanism which involves the transport of both ions and electrons.[12a,b] In this sense these materials have features in common with redox polymer modified electrodes and with electrodes of the second kind. They most strongly resemble certain transition metal oxides and sulfides which have been called intercalation compounds.[13]

Structure and Properties of the Transition Metal Hexacyanides

The structure of Prussian blue was first discussed by Keggin and Miles on the basis of powder diffraction patterns.[15] These authors distinguished between so-called soluble $KFeFe(CN)_6$ and insoluble $Fe_4(Fe(CN)_6)_3$ compounds. The former was presumed to form in the presence of excess potassium ion. The term soluble was invented by dye makers and refers to the ease with which the potassium salt can be peptized. For soluble PB the basic cubic structure consists of alternating iron(II) and iron(III) located on a face centered cubic lattice in such a way that the iron(III) ions are surrounded octahedrally by nitrogen atoms and iron(II) ions are surrounded by carbon atoms as shown in Figure 1. The potassium ions were presumed to occupy the octahedral interstitial lattice sites. The structure of insoluble PB was proposed to be basically the same except that excess ferric ion replaced potassium ion in the interstitial sites. These authors also discussed the reduced form of PB known as Everitt's salt $K_2FeFe(CN)_6$, and the oxidized form $FeFe(CN)_6$ referred to in the older literature as Berlin green.[8] The cubic unit cell dimensions of 10.2 Å were found to be the same, within experimental error, for all of these compounds. They also contain rather indefinite amounts of water. The dehydration of PB has recently been studied in some detail.[16]

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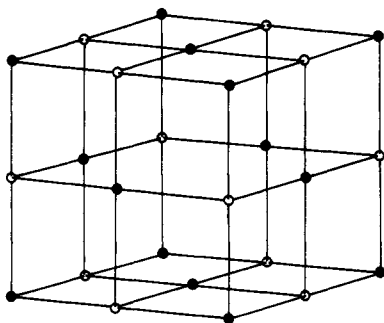
b

Figure 1. Illustrative depiction of the unit cells of Keggin and Miles structure ($\bullet$ Fe^{+3}; $\circ$ Fe^{II}).

The structure of insoluble PB has been determined from single crystals by Ludi et al.[18] The structure, which differs significantly from that of Keggin and Miles, is based on an accurate density as well as electron and neutron diffraction measurements. The PB structure is found to be similar to that of a whole class of transition metal cyanides studied extensively by Ludi and co-workers.[18] It is disordered, with one fourth of the ferrocyanide sites unoccupied, and no iron(III) ions are found in the interstitial sites.

The fact that PB is indeed ferric ferricyanide with weak field iron(III) coordinated to nitrogen and strong field iron(II) coordinated to carbon has been definitely established by Mossbauer and infrared studies.[6,14,19] The electronic spectrum of PB was discussed in a classic paper by Robin who also considered the ruthenium and osmium analogues.[20] The intense blue color is due to the charge transfer from iron(II) in a carbon hole to iron(III) in a nitrogen hole. The electron is approximately 98% localized on the ferrocyanide ion. According to the classification scheme of Robin and Day Prussian blue is a class II mixed-valence semiconductor.[6] The conductivity and activation energy have been measured for polycrystalline samples of PB but it should be emphasized that there is much to learn about electronic conduction in this class of compounds.[21-24,62]

The three-dimensional polymeric network which characterizes the transition metal hexacyanides is a unique feature among inorganic structures. In many respects these compounds resemble cross-linked organic polymers in terms of their low density, ready incorporation of solvent, and their variable structure and stoichiometry. They are known to be zeolitic in nature and readily exchange group I cations in aqueous solutions.[6-9] Also, like polymers, they are difficult to characterize. In fact, the chemical designation Prussian blue should be regarded as essentially a generic term for complex materials which may contain coprecipitated

or occluded ions, indefinite amounts of water, possibly hydrolyzed ferrocyanide, variable stoichiometry, and structural disorder.

Deposition of Transition Metal Hexacyanide Films

The formation of a thin film of PB on conducting or semiconducting substrates was first reported by Neff.[12a] At the same time it was shown that the PB deposit could be electrochemically oxidized or reduced. The films were prepared from a solution of $FeCl_3$ and $K_3Fe(CN)_6$ in excess KCl. The neutral red-brown complex $FeFe(CN)_6$ is formed in such solutions.[25-27] For some substrate materials such as Pt, Au, Al, or graphite, the PB films can be deposited by simply inserting the clean electrode in the ferric ferricyanide solution.

The deposition of PB on various substrates including transparent SnO_2 and TiO_2 has been studied most extensively by Itaya, et al.[28,29] They have introduced an electrochemical deposition which involves the reduction of $FeFe(CN)_6$ and leads to stable and reproducible films. They have also shown that the $FeFe(CN)_6$ complex in solution is a powerful oxidizing agent and that PB on the electrode surface is partially oxidized by this complex.[28c,29] The oxidizing power of $FeFe(CN)_6$ was first pointed out by DeWet and Rolle.[33]

The characterization of these microcrystalline deposits is subject to the same limitations as have been described for the bulk materials. The most conspicuous example of the difficulties in characterizing these materials is the fact that there is still not complete agreement, even among the authors themselves, concerning the stoichiometric composition. Neff, et al. have assumed that the soluble salt $KFeFe(CN)_6$ is formed in the presence of excess potassium ion.[12b,c] On the other hand Itaya et al. have found no evidence of potassium ion, based on ESCA and Auger spectra, in PB modified glassy carbon electrodes.[28c] Kuwana has also found no evidence for potassium ion in films analyzed by X-ray fluorescence spectroscopy.[30] These results have lead Itaya et al. to propose that insoluble PB is always formed in the deposition reaction.[28] Finally, Rosseinsky et al. have recently reported that insoluble PB, formed initially in the deposition reaction, is converted to the soluble form after cycling in the presence

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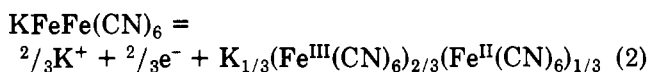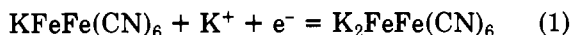*Itaya et al.*   Accounts of Chemical Research

of potassium ion.[31] Their results are based on the observation of a shift in the charge transfer band maximum for films which have been electrochemically cycled (i.e., oxidized and reduced).[31d] On the other hand, Itaya et al. show that the band shift is due to the fact that uncycled films are partially oxidized to Berlin green in the presence of the FeFe(CN)$_6$ complex in solution.[29,32] One might conclude that the results of chemical analyses should be unequivocal but, as we shall see, certain features of the electrochemical oxidation of PB are very difficult to understand without invoking the participation of potassium ions. In any event, the contradictions discussed above point to the need for very careful control of experimental conditions for the deposition reactions.

Other PB analogues, whose cations and anions form soluble complexes in their higher oxidation states, can also be deposited by electrochemical reduction. Ferric ruthenocyanide (ruthenium purple)[12c,28j] and ferric osmocyanide (osmium purple)[28k] have been deposited by electrochemical reduction of the corresponding ruthenicyanide and osmicyanide complexes in solution. Films of other analogues such as ferric carbonylpentacyanoferrate and ferric pentacyanonitroferrate have been prepared recently by the same methods.[34]

The synthesis of these films does not necessarily require a soluble solution complex which can be reduced. Siperko and Kuwana have studied the electrochemistry of a copper hexacyanoferrate film which was prepared voltammetrically by electroplating a thin film of copper on glassy carbon in the presence of ferricyanide ion.[35] Bocarsly et al. have prepared nickel hexacyanoferrate films by desolution of nickel in the presence of ferricyanide ions.[36] Silver hexacyanoferrate films can be formed by anodizing a silver wire in the presence of ferricyanide.[37] Crumbliss et al. have made an extensive study of PB deposits produced in an iron containing plasma formed from iron pentacarbonyl and ethane.[38] It is apparent that, with a certain amount of chemical ingenuity, we can expect to obtain many new types of surface-modified metal cyanides.

Electrochemical Reactions

Initially it was proposed that PB could be oxidized and reduced according to the following reactions:

$$KFeFe(CN)_6 + K^+ + e^- = K_2FeFe(CN)_6 \quad (1)$$

$$KFeFe(CN)_6 =$$
$$^2/_3K^+ + ^2/_3e^- + K_{1/3}(Fe^{III}(CN)_6)_{2/3}(Fe^{II}(CN)_6)_{1/3} \quad (2)$$

The mechanism was based on the results of voltammetric and spectral measurements and also on the assumption that the soluble form of PB is involved in the presence of excess potassium ion.[12b] A cyclic voltammogram of a PB film on a gold electrode in 1 N K$_2$SO$_4$

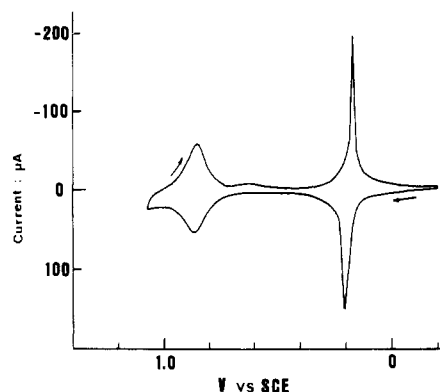(34) Itaya, K.; Sawaguchi, T.; Uchida, I., unpublished results.
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Figure 2. Voltammogram of PB film on a gold wire electrode in 1 N K$_2$SO$_4$ solution; sweep rate $v = 1$ mV/s.

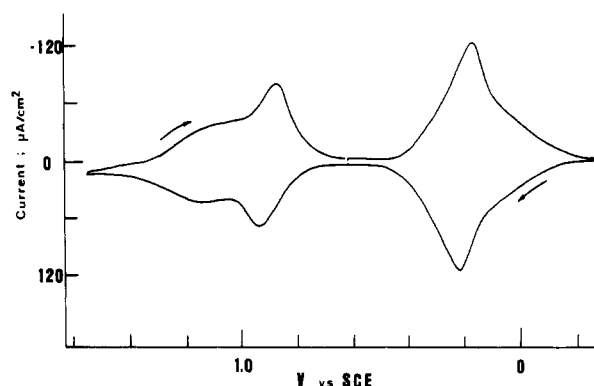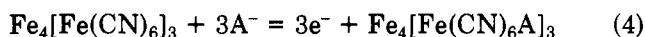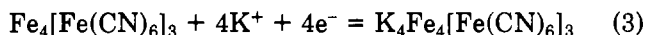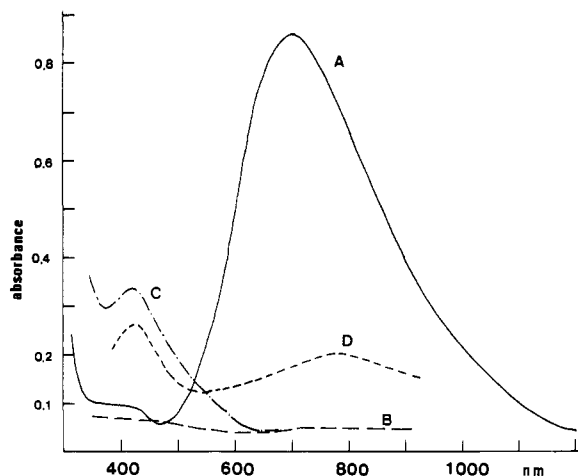**Figure 3.** Voltammogram of a PB film on a SnO$_2$ electrode in 1 N K$_2$SO$_4$ solution; sweep rate $v = 5$ mV/s.

solution is shown in Figure 2. The total charge consumed for the oxidation wave at 0.9 V (vs. SCE) was only approximately two-thirds of that consumed for the reduction at 0.2 V, and it was reported that Berlin green is actually a partially oxidized compound with the formula as shown in eq 2 above. It was noted that further oxidation of the film occured at potentials above 1.1 V but that, on the gold electrode, the film underwent irreversible decomposition at these potentials.

The reaction scheme shown above was questioned by Itaya et al. who found no potassium ion in their films as previously discussed.[28] They proposed the following scheme for the two reactions:

$$Fe_4[Fe(CN)_6]_3 + 4K^+ + 4e^- = K_4Fe_4[Fe(CN)_6]_3 \quad (3)$$

$$Fe_4[Fe(CN)_6]_3 + 3A^- = 3e^- + Fe_4[Fe(CN)_6A]_3 \quad (4)$$

In the oxidation reaction (4) the anion A$^-$ is supplied by the electrolyte. Equation 4 actually is meant to represent the complete oxidation which occurs in two steps at 0.9 and 1.2 V (vs. SCE).[28,32] Two distinct reversible waves were observed for a PB film on transparent tin oxide as shown in Figure 3. The stability of the reversible wave at 1.1 V is apparently due to the high overvoltage for oxidation of water (or electrolyte anions such as Cl$^-$) on the tin oxide. According to eq 3 and 4 the ratio of total charge consumed for the *complete* oxidation to that of the reduction would be 0.75. This result was obtained on tin oxide.[28c,i,32]

The completely oxidized form of PB is a yellow compound which cannot be prepared chemically in aqueous solution because of its high reduction potential. Its existence has been confirmed by spectroelectrochemical measurements.[28d,32] For example the charge transfer

Electrochemistry of Metal Cyanides

Figure 4. Absorption spectra obtained with a SnO_2 electrode with 10.5 mC/cm^2 of PB at different electrode potentials in 1 M KCl: (A) at 0.6 V vs. SCE, (B) at -0.2 V, (C) at 1.40 V, and (D) at 1.1 V. Reproduced with permission from ref 28c. Copyright 1982 American Chemical Society.

spectra of a PB film in various states of oxidation or reduction are shown in Figure 4. Detailed studies have revealed that the absorption maximum undergoes a frequency shift with a change in applied voltage.[32]

The fact that high-spin iron(III) is reduced and low-spin iron(II) is oxidized was established unequivocally by Itaya et al. on the basis of in situ Mössbauer measurements on iron 57 enriched PB films.[28d] The Mössbauer spectra of a single film at 0.6 and -0.2 V (vs. SCE) are shown in Figure 5. The measured quadrupole splittings and the isotope shifts indicate that the high-spin ferric ion is reduced. These results also confirm that electrochemically deposited PB, like the bulk material, is ferric ferrocyanide.

The existing uncertainty regarding the validity of reactions 1 and 2 vs. 3 and 4 is mainly due to the fact that potassium ion appears to be involved in both the reduction *and* the oxidation reactions. In order to discuss this point it is necessary to formulate the Nernst equation for these reactions. Spectral measurements indicate that these compounds undergo gradual and continuous change with a change in voltage, and it has been proposed that partially reduced or oxidized PB can be treated as a solid solution.[12b] In that event we can formally write a Nernst equation which, for example, for reaction 1 would have the form:

$$E = E^\circ + \frac{RT}{F} \ln \frac{a(PB)a(K^+)}{a(ES)} \qquad (5)$$

where $a(PB)$ and $a(ES)$ are the activities of Prussian blue and Everitt's salt respectively and $a(K^+)$ refers to the activity of the potassium ion in the solution phase adjacent to the film. Assuming the validity of eq 5, one would predict according to eq 1 and 2, that the voltammetric mid-peak potential would decrease with decreasing potassium ion concentration for *both* the oxidation and reduction reactions. This is exactly what is observed and, in fact, both reactions have a Nernstian slope of 59 mV over two orders of magnitude in KCl.[12b] On the other hand, reaction 4, involving as it does the participation of anions, should show an increase of midpeak potential with decreasing concentration of KCl. This is not observed at least in the first oxidation step. Itaya believes that the mechanism for the oxi-
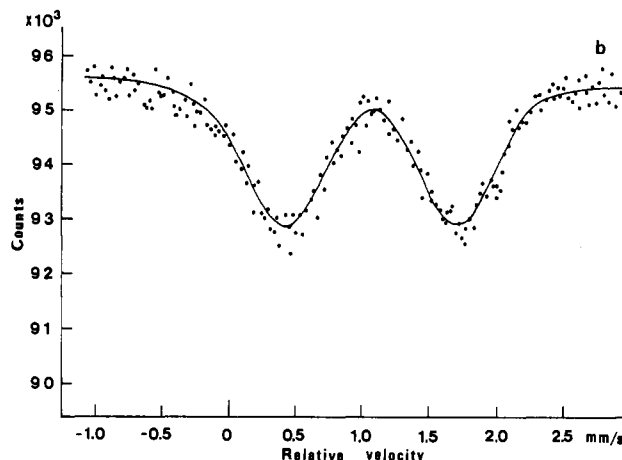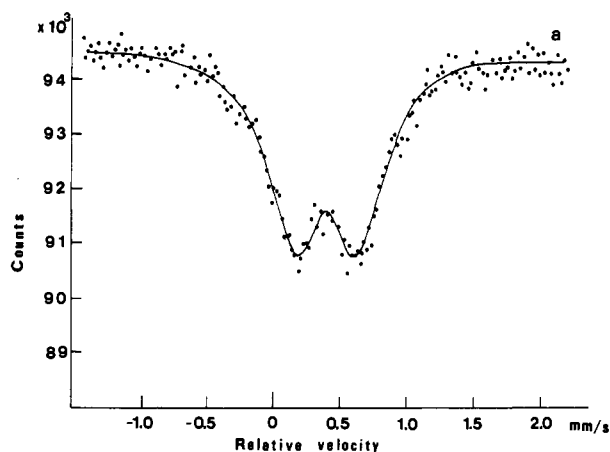

Figure 5. In situ Mössbauer spectra obtained at electrode potential at 0.6 V vs. SCE (a) and at -0.2 V (b). The isomer shift (δ) and the quadrupole splitting (ΔE) are 0.37 and 0.41 mm/s for the spectrum (a) and 1.14 and 1.13 mm/s for the spectrum (b), respectively. Reproduced with permission from ref 28d. Copyright 1982 American Chemical Society.

dation is quite complicated and may involve both cations and anions.[32]

The ability of cations, other than potassium, to penetrate the lattice has been of interest since the earliest investigations.[12b,26,28d] K^+, Rb^+, Cs^+, and NH_4^+ have been found to support sustained cyclic reactions. Repeated cycles are blocked in the presence of Na^+, Li^+, H^+, and all of the group II cations. The selective ion transport has been explained in terms of the hydratred ionic radii and the channel radius in the PB lattice. The channel radius of ca. 1.6 Å will accomodate K^+, Rb^+, Cs^+, and NH_4^+ whose radii are 1.25, 1.28, 1.19, and 1.25 Å, respectively. Electrostatic factors and ionic polarizabilities may also effect ion transport within the film. Crumbliss, et al. have recently examined alkali metal cation effects on a PB modified electrode obtained from an iron-containing plasma polymer.[38] They report that the electrode is permeable to Na^+ in contrast to results obtained with PB films. Although the reasons for the difference in behavior are not yet clear, it may be that ionic permeability is related to the lattice defects and structural disorder of the microcrystalline deposit. For example, it has been observed that Na^+ electroactivity persists for a longer number of cycles on PB films obtained at higher current densities.[28d]

Prussian blue may well become a model for the study of ion permeability. A detailed understanding of the thermodynamics and kinetics of ion transfer in PB films
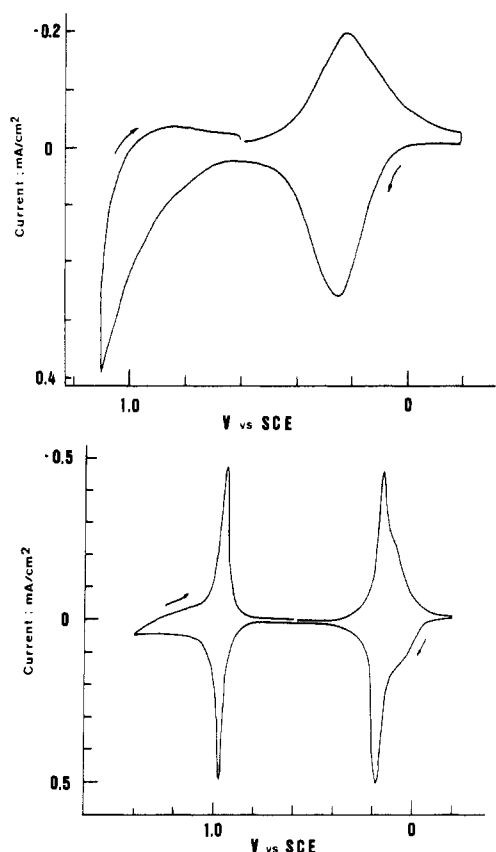
Figure 6. (a) Voltammogram of a ruthenium purple film on a Pt electrode in 1 N K_2SO_4 solution; sweep rate v = 20 mV/s. (b) Voltammogram of an osmium purple film on a SnO_2 electrode in 1 N K_2SO_4 solution; sweep rate v = 10 mV/s.

may be of considerable aid in the study of membranes in general and ion-selective electrodes in particular.[39,40] It is noteworthy that membranes of copper ferrocyanide have been employed for osmotic pressure measurements.[41]

Lastly, we consider the electrochemical reactions of some of the PB analogues. Ruthenium purple KFe-Ru(CN)₆ or Fe₄(Ru(CN)₆)₃ was the first compound to be studied after PB itself.[12b,28j] A voltammogram of ruthenium purple on Pt in 1 N K_2SO_4 is shown in Figure 6a. We note that the reduction of the high-spin Fe(III) occurs at approximately the same potential as its does in PB. There is, however, no corresponding oxidation wave. Apparently the reduction potential of $Ru(CN)_6^{-3}$ in this film is too high to be observed in an aqueous system.[28j] On the other hand, two well-developed waves are observed for the osmium analogue KFeOs(CN)₆ or Fe₄(Os(CN)₆)₃ as shown by the voltammogram in Figure 6b.[28k] Again the reduction of Fe(III) occurs at ca. the same potential as in PB indicating that ferric ions in the nitrogen holes are not much affected by the nature of the metal ions in the carbon holes. The similarity and the sharpness of both the oxidation and the reduction waves are also an interesting feature of osmium purple.

A single reversible wave has been observed by Siperko and Kuwana for copper hexacyanoferrate.[35] In this case

it has been shown that the electrochemical reaction involves the oxidation of the ferrocyanide ion at 0.7 V (vs. SCE) in 1 N KCl solutions. The proposed reaction is as follows:

$$K_2Cu_3(Fe(CN)_6)_2 = 2K^+ + 2e^- + Cu^3(Fe(CN)_6)_2 \quad (6)$$
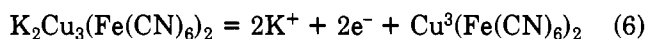
It was found that the midpeak potential for this reaction decreases, in Nernstian fashion, with decreasing potassium ion concentration. Sodium ion was found to block the reaction but these authors also made the remarkable observation that the total charge consumed in the electrolysis was proportional to the amount of potassium ion in mixtures containing sodium and potassium ions. This was true even though the amount of potassium ion present in all cases was more than sufficient to cause complete electrolysis of the film. This peculiar result is not presently understood.

Thermodynamic and Kinetic Factors

The shapes of the voltammograms for these reactions have been of considerable interest. For example, the voltammogram for the reduction of PB on Au or Pt electrodes is sharper than that obtained with tin oxide as shown in Figures 2 and 3. There may be variation of the shape even for films prepared on the same substrate depending on the rate of film deposition or on the film thickness.[28c] The nature of the electrolyte is also an important factor. For example, the voltammograms for the reduction of PB on gold electrodes are sharp in the presence of potassium ions and quite broad in the presence of ammonium ions. For ruthenium ferrocyanide films this situation is reversed.[12c]

The shapes of voltammograms obtained under reversible conditions at low-scan rates are often explained in terms of simple thermodynamic models invoking "interaction" energies. For example, this procedure is well known in the study of adsorbed species and the subject has been reviewed recently by Laviron.[42] Also, McKinnon and Haering have employed similar methods in a detailed treatment of the electrochemical thermodynamics of the intercalation compounds.[13] These authors use a lattice gas model in the mean field approximation and consider the possibility of long-range order. These theories have in common the fact that the electroactive material is treated as a one-component system. In the case of PB films Neff et al. have proposed that partially oxidized or reduced films be considered a two-component system (i.e., as a solid solution).[12b] If the solution is assumed to be strictly regular, the interaction energy is directly related to the heat of mixing and, depending on whether this is negative or positive, one obtains symmetrical broadening or narrowing of the voltammogram. The extreme limit of the latter would lead to an electrochemical phase transition (i.e., the analogue of phase separation in a liquid solution). Other factors which may affect the shapes of the voltammograms, such as structural disorder and the existance of multiple reaction sites, have not been studied in detail. Further understanding of the thermodynamics of PB electrochemistry is of interest not only of itself, but because this compound may be as close as we can come to the "ideal" model for the study of the intercalation reactions.

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The kinetics of these reactions are of considerable interest for the same reasons. For the oxidation and reduction of PB it has been shown that the electron transfer between the metal substrate and the polycrystalline film is the fastest of the transport processes.[12c] For all materials studied to date the peak currents and peak separations increase linearly with scan rate at low scan rates. At intermediate scan rates there is a gradual change to a square-root dependence of both peak current and peak separation. At very high scan rates or under pulse conditions, one must take account of chemical potential gradients within the film.[12b] In many respects the transport kinetics are similar to the case of redox polymer modified electrodes.[1b,43-46] Neff et al. have carried out a kinetic study of PB and RP under pulsed conditions taking into account both migration and diffusion of potassium ions with finite boundary conditions. The transient behavior is formulated in terms of the Nernst–Planck equation. Yap et al. have carried out a similar analysis for polymer modified electrodes. Their numerical solution of the transport equations allows consideration of the short time current behavior.[47] Itaya et al. have recently studied the short time behavior of PB films and have found large migration effects for the reduction of PB but not for the reoxidation of ES.[48] DeBerry and Viehbeck have also studied diffusion in PB films.[56] Finally, Murray et al. have recently reported extremely interesting measurements of steady state dc electron conductivity in PB films on an interdigitated platinum array electrode. They find that the half-maximal dc current is displaced cathodically to the formal potential for the reduction of PB.[63]

Electrocatalysis

It is natural to consider possible electrocatalytic applications of the transition metal hexacyanides. The catalytic reduction of oxygen dissolved in a PB film has been reported by Itaya et al.[28g,h] It was found that Everitt's salt reduces both molecular oxygen and hydrogen peroxide. It was also reported that the oxidized compounds (i.e., Berlin green or Prussian yellow) are good catalysts for the oxidation of hydrogen peroxide. The authors have suggested that the O_2 molecules migrate to the ferrocyanide vacancies (see Figure 1b) where they are in a position to accept four electrons more or less simultaneously from the surrounding iron(II) ions in Everitt's salt.

Cox and Kulesza have discovered how to deposit very thin films of ruthenic ruthenocyanide on glassy carbon.[51] They have reported that these films show remarkable electrocatalytic activity for the oxidation of arsenic(III). The ruthenium modified electrodes show great stability and retain catalytic activity for long periods even after exposure to air.

Ogura et al. have recently reported catalytic activity for the reduction of CO to methanol on PB electrodes.[52] It is reasonable to assume that further studies will reveal a variety of interesting catalytic effects.

Applications

The chemical stability, bichromic reactions, ease of preparation, and low cost of PB modified electrodes makes them obvious candidates for application in electrochromic displays. Such an application has been described by Itaya et al.[28a] They have reported that color switching for the reduction to Everitt's salt is stable up to 10^7 cycles for PB on a SnO_2 substrate.[28e] Further developments have been recently described by Ataka et al.[53] Since such devices depend on electron and ion transport, the switching times depend on voltage and the amount of material on the electrodes. Under the best conditions it appears that switching times may be comparable with those of liquid crystal displays. For practical applications certain obvious problems must be overcome. For example, although PB and many of its analogues are highly stable compounds, the oxidized or reduced forms often are not. Everitt's salt slowly reverts to PB in aqueous solution containing dissolved oxygen. Berlin green and Prussian yellow also revert to PB in aqueous solution under open circuit conditions. These compounds may oxidize solution impurities or possibly the solvent. Obvious alternatives are to try more stable solvents although little work along these lines has been reported.

It is also obvious that PB and related compounds may be considered for energy storage and battery applications.[54,55] Although the PB battery has a low energy density it has advantages due to its low cost and the highly reversible nature of the electrode reactions.

As in the case of any electroactive semiconductor, it is natural to consider photovoltaic or photoelectrochemical effects with PB films deposited on metals or other semiconductors. Up to now no direct photovoltaic effect has been reported for PB films. This may be due to the highly defective structure of PB which would tend to destabilize photoinduced electron-hole pairs. Indirect photo effects have, however, been observed by DeBerry and Viehbeck who reported on the photoinduced oxidation of Everitt's salt deposited on *n*-type titanium dioxide.[56] This effect has also been studied in greater detail by Itaya et al. who found that both Everitt's salt and PB can be photooxidized on TiO_2

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electrodes.[28i] It has been determined that the photoactive material is the titanium dioxide. The authors have suggested that this photoelectrochromic effect may find application in an erasable optical signal recording system.

Bocarsly et al. have recently reported that semiconductors such as cadmium sulfide are dramatically stabilized against corrosion in the presence of ferrocyanides due to the formation of insoluble cadmium cyanoferrates at the surface.[57] Kaneko et al. have used a dispersion of Prussian blue and a ruthenium complex to carry out photolysis of water.[58] It is interesting to note also that PB films have recently been used as a standard for ellipsometry and Fourier transform photoacoustic spectroscopy.[38d,60,61]

Concluding Comments

We have attempted to describe some new electrochemical perspectives in relation to some very old materials. It has been emphasized that the electrochemical behavior of the prototype compound itself is not fully understood. The structure, stoichiometry, ionic permeability, and electrochemical reactions of PB films deserve further consideration.

We have also attempted to describe the electrochemistry of a few of the cyano analogues of PB. This is a huge class of compounds and they are not all cubic. There are insoluble planar sheet-like structures (e.g., nickel) and linear structures (e.g., silver).[10] We anticipate that a large number of new modified electrode polynuclear cyano complexes will be studied in the near future.

Finally, we have noted a few recent applications of these materials. Here we believe there is great potential for future development. The chemical stability, ease of preparation, and low cost of many metal cyano films are important factors which may lead to a variety of new applications in electrochemistry, electrooptics, and electronics.

Registry No. Prussian blue, 12240-15-2.

Carbohydrate Liquid Crystals

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Lyotropic liquid crystal behavior is of interest to molecular biologists because of the amphiphilic chemical constitution of membrane components. As the name implies, this is a dissolution property. The implication that liquid crystal phase transitions play an important role in the organization and functioning of cells and tissues is long-standing.[1-3] *Thermotropic* liquid crystal behavior is a solid-state phenomenon caused by the application of heat. It is of particular interest to physicists,[4] since it forms the basis of electrooptical devices. Recently the liquid crystalline state has become important in polymer physics because of its role in the manufacture of high-performance fibres.[5]

Because carbohydrate chemists are neither molecular biologists nor solid-state physicists, they have been slow to exploit their potential for synthesizing a very large number of carbohydrates which have liquid crystal properties. A few n-alkyl 1-O-glycosides are available from commercial sources because they are used as detergents for cell wall membranes.[6-8] Some n-alkyl 1-S-glycosides have been synthesized because of their potential for selectively affecting cell surfaces and for use as enzyme substrates.[9-11]

Emil Fischer in 1911 noted the *double melting point* of some long-chain n-alkyl pyranosides,[12] and, in 1938, this was recognized as evidence for the formation of thermotropic liquid crystals,[13] but until recently there has been no sustained interest.

No carbohydrates were included in a compendium of 7000 thermotropic liquid crystals, published in 1973.[14] Of the more than 5000 references under the liquid crystal descriptor in the *Chemical Abstracts* Indices from 1976 to 1981, there is only one to the alkyl glucopyranosides.[15]

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