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Spectroelectrochemistry and Electrochemical Preparation Method of Prussian Blue Modified Electrodes

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Abstract: The details of a preparation method for Prussian blue (PB) film on electrodes are discussed. The electrochemistry of the PB-modified electrodes is examined in solutions of various supporting electrolytes. K^+, Rb^+, NH_4^+, and Cs^+ can be expected to transport through the crystal of PB because of its zeolitic nature. A spectroelectrochemical study shows the values of molar extinction coefficient and the absorption spectrum of the fully oxidized form of Prussian blue. The structure of the PB film prepared by an electrochemical method is formulated as a "water-insoluble PB", $Fe_4^{III}[Fe^{II}(CN)_6]_3$. The chemical deposition of PB is also discussed.

Prussian blue (PB) has been manufactured as an important pigment for paints, lacquers, printing inks, and other color uses.[1] As is well-known, there are two proposed formulas of PB, which have been called "water-insoluble PB" ($Fe_4^{III}[Fe^{II}(CN)_6]_3$) and "water-soluble PB" ($KFe^{III}Fe^{II}(CN)_6$).[2–4] That this pigment is an iron(III) hexacyanoferrate(II) has been definitely shown by observations on the infrared absorption spectrum,[5] the Mössbauer resonance spectrum,[6,7] and the optical absorption spectra.[3,8]

It has been also shown that chemical reduction and oxidation of PB can lead to Prussian white (Everitt's salt) and Prussian green (Berlin green), respectively.[4] The crystal structure of PB originally proposed by Keggin and Miles[9] is the cubic face-centered type, with a lattice constant of about 10 Å. In the case of "water-insoluble PB" ($Fe_4^{III}[Fe^{II}(CN)_6]_3$), the model proposed that the two fourfold positions, ($^1/_4$, $^1/_4$, $^1/_4$) and ($^3/_4$, $^3/_4$, $^3/_4$), were occupied by the required number, $^4/_3$, of Fe^{III}. Ludi et al. have proposed a new modified structure for PB analogues that discards the assumption of the existence of interstitial Fe^{III}.[2] A recent paper has proved the existence of two structurally distinguishable water molecules by a neutron-diffraction study, indicating vacancies of $Fe^{II}(CN)_6$.[10]

Although PB has long been an important pigment, the electrochemistry of PB has not yet been fully investigated. This might be due to lack of knowledge of techniques for the preparation of the thin-film form on substrates.

Recently, reports by Neff et al. have briefly shown a method of preparation of a thin film of PB on platinum (Pt) and gold (Au) electrodes and demonstrated the redox behavior of PB.[11,12] Although mechanistic studies of the chemical synthesis of PB demonstrated by Neff[11] have not been reported yet, we have recently disclosed a new method of preparation for PB films of high quality and reported the electrochemistry[13] and its application in a very stable electrochromic device.[14] In this paper, the details of the preparation method proposed by us and the electrochemistry of the resulting PB film are discussed. In addition to our procedure, chemical synthesis of PB is also discussed.

Experimental Section

$K_3Fe(CN)_6$ was purified by two recrystallizations. An $FeCl_3$ solution was prepared by dissolving a measured amount of a standard iron wire (99.99%) in a small volume of hot hydrochloric acid (HCl). Excess HCl was removed by repeatedly evaporating at the boiling point and adding distilled water, until the pH was 2.0. Lithium chloride, sodium chloride, potassium chloride, rubidium chloride, cesium chloride, ammonium chloride, barium chloride, and tetraethylammonium perchlorate (TEAP) were all reagent grade and were used without purification.

As documented in previous papers,[12,14] the chemical method and the electrochemical method of preparation were strongly affected by the nature of the substrate surface. It has been particularly pointed out in our previous paper that reducible organic substances could be the reducing agents for the chemical synthesis of PB in a solution of ferric ferricyanide.[14] Organic substances such as epoxy resins, commercial rubbers, and plastics were so rapidly covered by PB that they could not be used as the materials for the electrode mounting. We noticed that strongly adherent films could not be formed even on disk electrodes mounted in a Teflon rod. The adhesion of the film was more critically important in the oxidation of PB than in the reduction. The film with poor adhesion was easily removed in the oxidation of PB, although the film was fairly stable during the repetition of the reduction of PB. For this reason, electrodes of Pt, glassy carbon (GC) (Tokai Carbon Co.), and gold (Au) were used as disk electrodes mounted in glass tubes. A strip of SnO_2 electrode (Corning, 10 Ω/grid) was used with an ohmic contact wrapped with a Pt wire. Only half of the strip of SnO_2 was immersed into the solution. Pt, GC, and Au electrodes were first polished with alumina slurry (particle size 0.05 μm). The electrodes were immersed in concentrated sulfuric acid for 1 h before use.

The film of PB on the electrodes was prepared in an aqueous ferric ferricyanide solution of an equivolume mixture of 20 mM $FeCl_3$ (pH 2.0) and 20 mM $K_3Fe(CN)_6$ in 0.01 M HCl. The working electrodes were cathodically polarized in the above ferric ferricyanide solution by means of a galvanostatic condition. A large Pt foil (5 cm^2) was used as a counterelectrode. The electrodes, after the deposition of a certain amount of PB, were thoroughly rinsed in 0.01 M HCl for 10 min. Anhydrous PB films on the electrodes tended to form cracks that could be observed in an SEM. For this reason, the electrodes with PB film were used without a drying procedure.

Voltammograms were obtained with a PAR (Princeton Applied Research) Model 174 instrument equipped with a Model 179 digital coulometer. A saturated calomel electrode (SCE) was used as the reference electrode. Because the reduced form of PB is sensitive to oxygen, the measurement must be done in an oxygen-free solution. The cell was purged with pure nitrogen gas. The apparatus used for the spectroelectrochemical studies was almost the same as that designed by Kuwana et al.[15] The absorption spectra were obtained with a Hitachi Model 330 spectrometer. Auger and ESCA electron analyses of PB on a GC electrode were carried out with Physical Electronics Model 548 equipment.

The elemental analysis for the contents of iron and potassium in the PB film was performed with an atomic absorption spectrophotometer,

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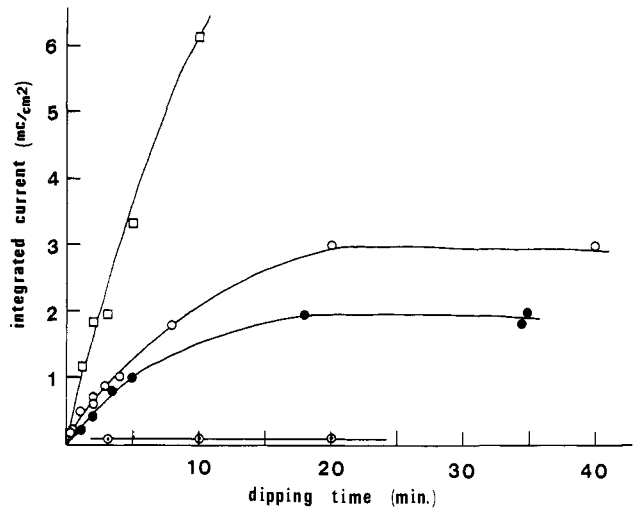

Figure 1. The rate of deposition of PB by a nonelectrochemical method on various substrates in a solution of an equivolume mixture of 20 mM $FeCl_3$ (pH 2.0) and 20 mM $K_3Fe(CN)_6$ in 0.01 M HCl. (□) Gold electrode; (○) platinum electrode; (●) glassy carbon electrode; (⊙) SnO_2 electrode.

Seiko Model SAS-725. An electrochemically prepared PB film on a platinum foil electrode (10 cm²) was decomposed by 28% aqueous ammonia and then acidified by 6 M HCl. The total volume of the solution including the decomposed PB was 100 mL.

Results and Discussion

Formation of PB by a Nonelectrochemical Method. Neff et al. have shown a method for the preparation of PB films on Pt and Au electrodes.[11,12] The electrodes were simply immersed in a solution of ferric ferricyanide for a certain period of time. As has been pointed out by Neff et al.[11,12] and by us,[14] the data obtained by this method was very dependent on the nature of the substrate surface. We found that "reducible organic substances" on the electrode surface strongly affected the reproducibility of the data. For this reason, the electrodes used in the present study were all disks sealed in glass tubes except the SnO_2 electrode. With the precautions described in the Experimental Section, reproducible results could be obtained.

Figure 1 shows the rate of chemical formation of PB. The cleaned disk electrodes and an SnO_2 plate were immersed in the solution of ferric ferricyanide, and then the electrodes were throughly rinsed in 0.01 M HCl for 10 min. The amount of deposition of PB was measured by coulometry. The electrode potential was scanned from 0.6 to −0.2 V at 50 mV/s. During this scan, the total amount of charge consummed by the reduction of the deposit was measured.

The deposition rate on an Au electrode was very fast in comparison with those on the other substrates. Pt and GC electrodes showed almost the same rate of deposition. No further increase was observed after 20 min on Pt and GC electrodes. A very small amount of deposition, less than 0.08 mC/cm², was found on an SnO_2 electrode at the start of immersion, but it did not increase at all.

Although a mechanistic study of the chemical reaction would be of special interest, we found that GC, Pt, and SnO_2 electrodes examined here showed very positive open-circuit potentials in the solution of ferric ferricyanide. For example, about 0.85 V vs. SCE was observed just after the immersion of a Pt electrode, and this increased to 0.98 V vs. SCE during about 40 min. This observation seems to be an important aspect of the mechanism of deposition. Such a very positive open-circuit potential could be obtained in neither a solution of $FeCl_3$ nor of $K_3Fe(CN)_6$, suggesting that the mixture of the solutions of $FeCl_3$ and $K_3Fe(CN)_6$ is a very strong oxidant. This is probably the reason that any contaminations of "reducible substances" on the electrode surface caused a large amount of deposition.

The oxidation of the electrodes themselves, formation of oxides or dissolution, are possible at the potential observed in the solution of ferric ferricyanide.[15,16] This is probably the mechanism of the chemical reaction. An SnO_2 electrode cannot be further oxidized.[15] This seems to be the reason that only a small amount of deposition was observed on the SnO_2 electrode. A separate experiment was carried out on a platinum oxide covered Pt electrode. A Pt electrode was oxidized at 1.0 V vs. SCE in 0.1 N H_2SO_4 for 1 min, and then it was immersed in the solution of ferric ferricyanide for 10 min. No deposition was detected by the coulometric method described above.

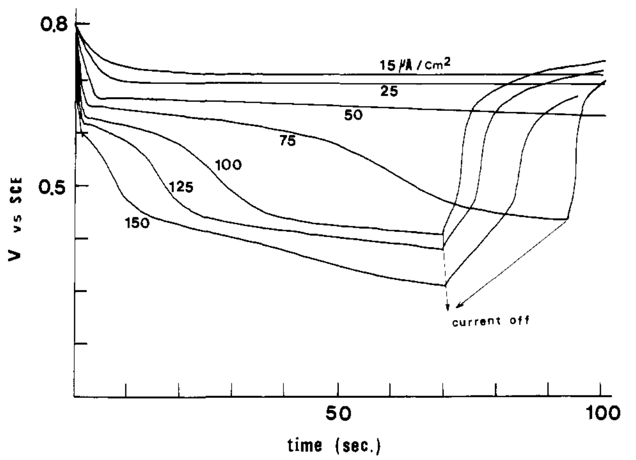

Figure 2. Galvanostatic transient behavior of a Pt electrode in a solution of an equivolume mixture of 20 mM $FeCl_3$ and 20 mM $K_3Fe(CN)_6$ at different current densities.

For pretreatment of the electrodes, a Pt electrode was cathodized in 1 M HCl for 15 min at 0.1 mA/cm², which was exactly the same as Neff's procedure,[11,12] and then the electrode was immersed in the solution for certain periods of time. Exactly the same amount of PB was deposited, indicating that there was no merit in the above procedure.

Finally, it is noteworthy that the 0.98 V observed open-circuit potential is very near to the onset of the reduction wave of the oxidized form of PB as is shown in Figure 2. This strongly suggests that the deposit obtained by the nonelectroplating method cannot be PB because PB is oxidized at this potential.

Electrochemical Deposition of PB. As shown in Figure 1, an SnO_2 electrode could not be covered by PB deposit. This would be desirable due to the importance of SnO_2 electrodes in spectroelectrochemical studies and in practical applications such as electrochromic displays. Besides this, a Pt electrode could only acquire a film of 3–4 mC/cm². This was visually only slightly blue. Instead of the nonelectroplating method discussed above, an electrochemical method has been proposed in our previous paper.[13,14] Figure 2 shows the galvanostatic transient behavior of a Pt electrode in a solution of ferric ferricyanide. The electrode potential was monitored against the SCE reference electrode. At the lower current density, less than 50 μA/cm², only a plateau was observed at about 0.7 V. The second plateau was clearly observed at about 0.4 V with the higher current density. The half-wave potentials for reduction of $FeCl_3$ and $K_3Fe(CN)_6$ were obtained at about 0.5 and 0.2 V vs. SCE in a solution of 0.1 M KCl and 0.01 M HCl, respectively. The second plateau observed in Figure 2 is certainly due to the reduction of Fe^{III} in the solution of ferric ferricyanide. The first plateau could not be observed in the solutions of $FeCl_3$ and of $K_3Fe(CN)_6$ alone. Note that the cyclic voltammogram was obtained in an aqueous ferric ferricyanide solution of an equivolume mixture of 0.1 M $FeCl_3$ and 0.1 M $K_3Fe(CN)_6$ in 0.1 M HCl, yielding an irreversible new wave commencing at about 0.7 V vs. SCE, which was just at the onset of the oxidation wave of PB. The first plateau in Figure 2 might be due to the reduction of a new redox couple formed in the solution of ferric ferricyanide. The formation of a one-to-one complex, $Fe^{III}–Fe^{III}(CN)_6$, between ferric and ferricyanide ions

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has been studied,[17-19] and this may be important in the electrochemical deposition of PB as well as in the nonelectroplating deposition.

A blue color could be seen at the start of the electrolysis due to the formation of the PB film on the electrode surface. As long as the electrode potential was kept at the first plateau, the blue color could only be formed on the electrode surface. No diffusion of the blue color into the solution was observed. On the other hand, once the electrode potential was at the second plateau, a blue cloud was formed in the solution. In this potential region, the reduction of Fe^{III} is a diffusion-controlled process, so that mutual encountering of Fe^{II} and $Fe^{III}(CN)_6$ in the solution is expected, yielding the bulk precipitation of PB. For the preparation of PB thin films on substrates, the electrode potential must be more positive than 0.5 V vs. SCE. It must be emphasized that the electrode potential obtained at the first plateau, about 0.7 V vs. SCE, suggests that the deposit is PB, not the oxidized form of PB. This seems to be a remarkable difference from the chemical formation discussed above.

It is noteworthy that the open-circuit potentials observed in Figure 2 increased very rapidly to more positive potential than 0.7 V vs. SCE. These potentials increased to about 1.0 V vs. SCE during 10 min. As discussed above, it is strongly suggested that the PB deposit, prepared by the electrochemical method, can be chemically oxidized to Berlin green in the solution of ferric ferricyanide.

Electrochemistry of PB-Modified Electrodes. A brief study of the electrochemistry of PB, prepared by the chemical deposition method, was recently published by Ellis et al.[12] We found that the voltammogram of PB-modified electrodes depended on the current density used for the preparation of the PB film. Two distinctly different voltammograms were observed.

Figure 3A shows the cyclic voltammograms of a PB-modified Pt electrode in 1 M KCl (pH 4.0). The film of PB was prepared at a lower current density of 10 $\mu A/cm^2$ for 400 s. The shape of the voltammogram is somewhat similar to that reported by Neff.[11] However, the waves at 0.2 V are much more symmetrical, with almost zero peak-potential separation. The half-widths, about 180 mV, were almost the same in both directions of the current. Although the peak currents at 0.2 V increased about 5% during the repeated scan, a steady voltammogram was achieved after about five cycles, as shown in Figure 3A. The peak current depended directly on the scan rate of the electrode potential up to 1 V/s, indicating that the electron-transfer reaction in the film is very fast. Very fast current responses (less than 100 ms) have been recorded by stepping the electrode potential between 0.6 and −0.3 V, with a 0.5-s pulse duration.[13] The total amount of charge consumed at the reduction of PB was 5 mC/cm^2, which was larger than the charge used for the preparation of the film of PB (4 mC/cm^2). This result showed that the efficiency for the deposition of PB exceeded 100% but depended on the current density, the concentration of the ferric ferricyanide, and the period of time of electrolysis.

The stability of the wave at 0.2 V was excellent. A lifetime experiment showed that only 5–10% decrease in the total charge was observed after 5×10^6 cycles at 5 Hz, stepping the electrode potential between 0.6 and −0.2 V vs. SCE. Because the reduced form of PB was sensitive to oxygen, the bubbling of oxygen into a cell caused an autooxidation of the reduced form of PB (Prussian white) to PB. A preliminary experiment showed that the reduced form of PB film (5 mC/cm^2) on the SnO_2 electrode was oxidized to PB in oxygen-saturated 1 M KCl (pH 4) solution within 20–30 min. However, the reduced form of PB was very stable in a nitrogen-bubbled solution. No increase in the absorbance at 700 nm was observed when the reduced PB film was allowed to stand in oxygen-free 1 M KCl for 5 h.

The oxidation wave of PB observed at about 0.9 V had a less symmetric nature. The peak currents were directly proportional to the scan rate up to 200 mV/s, suggesting that the rate of the electron-transfer reaction observed at 0.9 V was slower than that at 0.2 V.

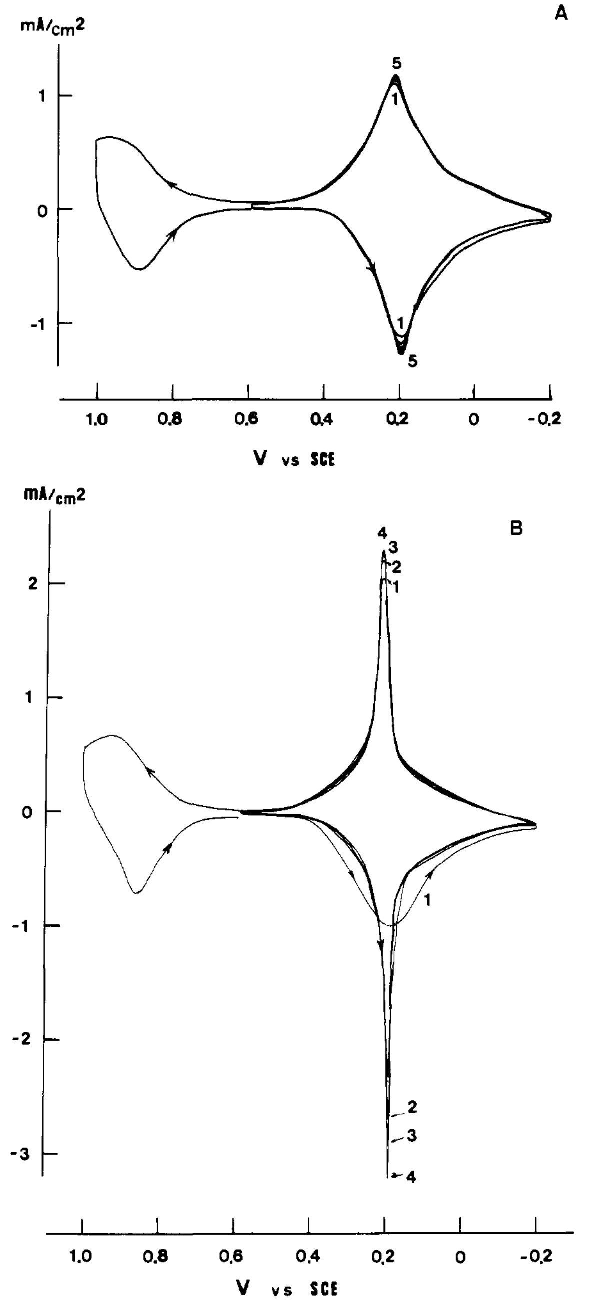

Figure 3. (A) Cyclic voltammograms of a PB-modified Pt electrode with 5 mC/cm^2 as the total charge consumed in the reduction of PB, prepared at a current density of 10 $\mu A/cm^2$ for 400 s. (B) Cyclic voltammograms of a PB-modified electrode, prepared at a current density of 100 $\mu A/cm^2$ for 50 s. The number in the figure shows the repeated cycle between 0.6 and −0.2 V. After the scan was repeated 5 times, the oxidation waves at 0.9 V were recorded. In both cases, the electrode potential was scanned at 20 mV/s. The solution used was 1.0 M KCl (pH 4.0) and was purged with pure nitrogen gas.

Figure 3B shows voltammograms obtained at a PB-modified Pt electrode prepared at a higher current density (100 $\mu A/cm^2$) for 50 s in a stirred solution. The first scan from 0.6 to −0.2 V showed a voltammogram similar to that in Figure 3A. However, a very sharp oxidation wave was observed in the reverse scan. Interestingly, the reduction wave of PB showed a sharp spike on the second scan. Such very sharp currents grew during repeated scanning, consuming the side wings of the wave. These sharp peaks with a half-width of about 40 mV and peak separation of about 10 mV depended slightly on the scan rate and the amount of PB. A steady voltammogram was again obtained after 5–10 cycles.

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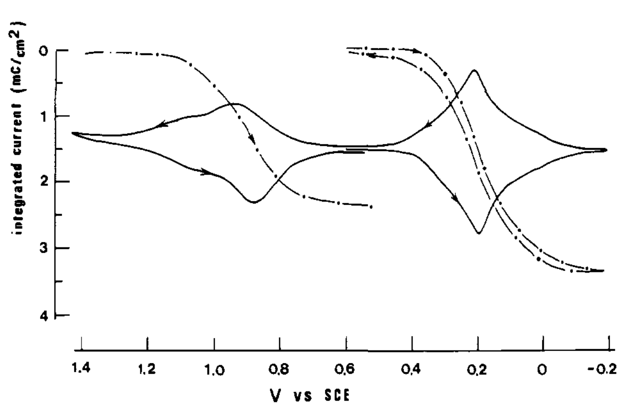

Figure 4. Cyclic voltammograms of a PB-modified SnO_2 electrode with 3.3 mC/cm² as the total charge consummed in the reduction of PB, prepared at a current density of 10 μA/cm². The scan rate was 20 mV/s. The solution was 1.0 M KCl (pH 4.0). The dashed lines show the integrated currents in the waves at 0.2 and 0.9 V.

A similar voltammogram has been reported on an Au electrode.[12]

Such sharp spikes have been frequently observed on polymer-modified electrodes.[20-23] Because the structures of polymers seem to be strongly affected by the degree of redox reactions, swelling, and so on, a structural change is the probable reason for the sharp spike in the case of polymer-modified electrodes.[20,21]

However, PB is a three-dimensional crystal, and the dimension of the unit cell of the reduced form of PB is the same as that of PB.[24] A structural change does not seem to be the reason for the appearance of the spike. Ellis et al. proposed an explanation for this behavior on the basis of a theory of regular solutions.[12] However, we have already indicated that the sharp spike could not be observed on the film prepared at a lower current density as shown in Figure 3A. A SEM of a film prepared at the lower current density revealed a uniform film structure with the expected thickness. On the other hand, a SEM of a film prepared at the higher current density showed a somewhat rough surface structure, although it was still a quite uniform thickness over the substrate surface. Therefore, no positive observation was achieved as an explanation of the sharp spike.

A brief observation of the mediated electron-transfer reactions of $Fe^{2+/3+}$ and $Fe(CN)_6^{4-/3-}$ on a PB-modified electrode showed that the reduction of Fe^{3+} commenced at about 0.3 V, which was less positive than the onset of the reduction of PB (0.4 V), but no oxidation wave was obtained because of the redox potential of $Fe^{2+/3+}$ (about 0.5 V vs. SCE). Both the reduction and oxidation of $Fe(CN)_6^{4-/3-}$ could be mediated by the redox reaction of PB. These results suggest that the film prepared at a higher current density could include uncoordinated $Fe(CN)_6^{4-/3-}$ and $Fe^{2+/3+}$ ions, and this seems to be the reason for the current spike. Coulometry performed during cyclic voltammetry between 0.6 and −0.2 V indicated that less than 5% of the total amount of the charge recorded at the first scan was lost in a few repeated scans for the film prepared at the lower current density. An amount of 15–20% was lost for the film obtained at the higher current density. This is an indication that the film prepared at higher current densities has a fairly large amount of uncoordinated ions. The wave observed at 0.9 V was almost the same as that shown in Figure 3A.

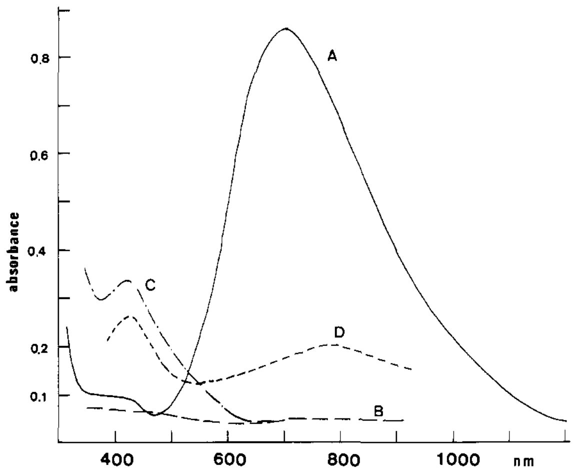

Figure 5. Absorption spectra obtained with an SnO_2 electrode with 10.5 mC/cm² of PB at different electrode potentials in 1.0 M KCl (pH 4.0). (A) At 0.6 V vs. SCE; (B) at −0.2 V; (C) at 1.40 V; (D) at 1.1 V.

It is noteworthy that the amount of PB can be controlled up to 50 mC/cm² or even more by changing the current density and the time of electrolysis. The dependence of the electrochemistry on the film thickness is of special interest.

Stoichiometry of PB. There are two proposed formulas of PB that have been called "water-insoluble PB", $Fe_4^{III}[Fe^{II}(CN)_6]_3$, and "water soluble PB", $KFe^{III}Fe^{II}(CN)_6$. The sparse published analytical data, however, indicate that potassium has to be considered as an impurity of the colloidal PB.[2] Ludi and Güdel suggested that the water-soluble PB were nonstoichiometric compounds rather than compounds showing a definite formulas.[2] The electrochemical reaction mechanism of PB is dependent on the formula of PB. The possible mechanisms for the waves are formulated as follows (depending on the formula), where A^- waves at 0.2 V represents the anion of supporting electrolytes.

waves at 0.2 V

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4e + 4K^+ \rightleftharpoons K_4Fe_4^{II}[Fe^{II}(CN)_6]_3 \ldots \quad (1)$$

$$KFe^{III}Fe^{II}(CN)_6 + e + K^+ \rightleftharpoons K_2Fe^{II}Fe^{II}(CN)_6 \ldots \quad (2)$$

waves at 0.9 V

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 - 3e + 3A^- \rightleftharpoons Fe_4^{III}[Fe^{III}(CN)_6A^-]_3 \ldots \quad (3)$$

$$KFe^{III}Fe^{II}(CN)_6 - e - K^+ \rightleftharpoons Fe^{III}Fe^{III}(CN)_6 \ldots \quad (4)$$

We have recently represented the Mössbauer effect measurement on the electrochemically prepared PB with an in situ method.[29] The film of PB on glassy carbon disks was obtained in an aqueous ferric ferricyanide solution of an equivolume mixture of 20 mM $^{57}FeCl_3$ (95.2% enriched) and 20 mM $K_3Fe(CN)_6$ in 0.01 M HCl. The isomer shift and the quadrupole splitting were 0.37 mm/s and 0.41 mm/s, respectively, for the Mössbauer spectrum obtained at 0.6 V vs. SCE. The absorption was easily interpreted as coming from the trivalent high-spin iron ions (Fe^{III}) in PB. For the spectrum obtained at −0.2 V vs. SCE, the isomer shift and the quadrupole splitting were 1.14 mm/s and 1.13 mm/s, respectively. The above result indicates directly that only the high-spin Fe^{III} ions are quantitatively reduced to the high-spin Fe^{II} ions through the electrochemical reaction (eq 1 or 2).[29]

Ellis et al. assumed that the deposit obtained by a nonelectroplating method was water-soluble PB.[12] We have been particularly concerned with the existence of potassium ions in films prepared electrochemically. An ESCA spectrum of a PB-modified GC electrode (film thickness about 2000 Å) showed no potassium band at 295 eV, $2P_{3/2}$, for its binding energy, and an Auger spectrum showed no band at 252 eV. Kuwana has observed no existence of potassium ions in the film by means of X-ray fluorescence spectroscopy, in agreement with our observation.[28]

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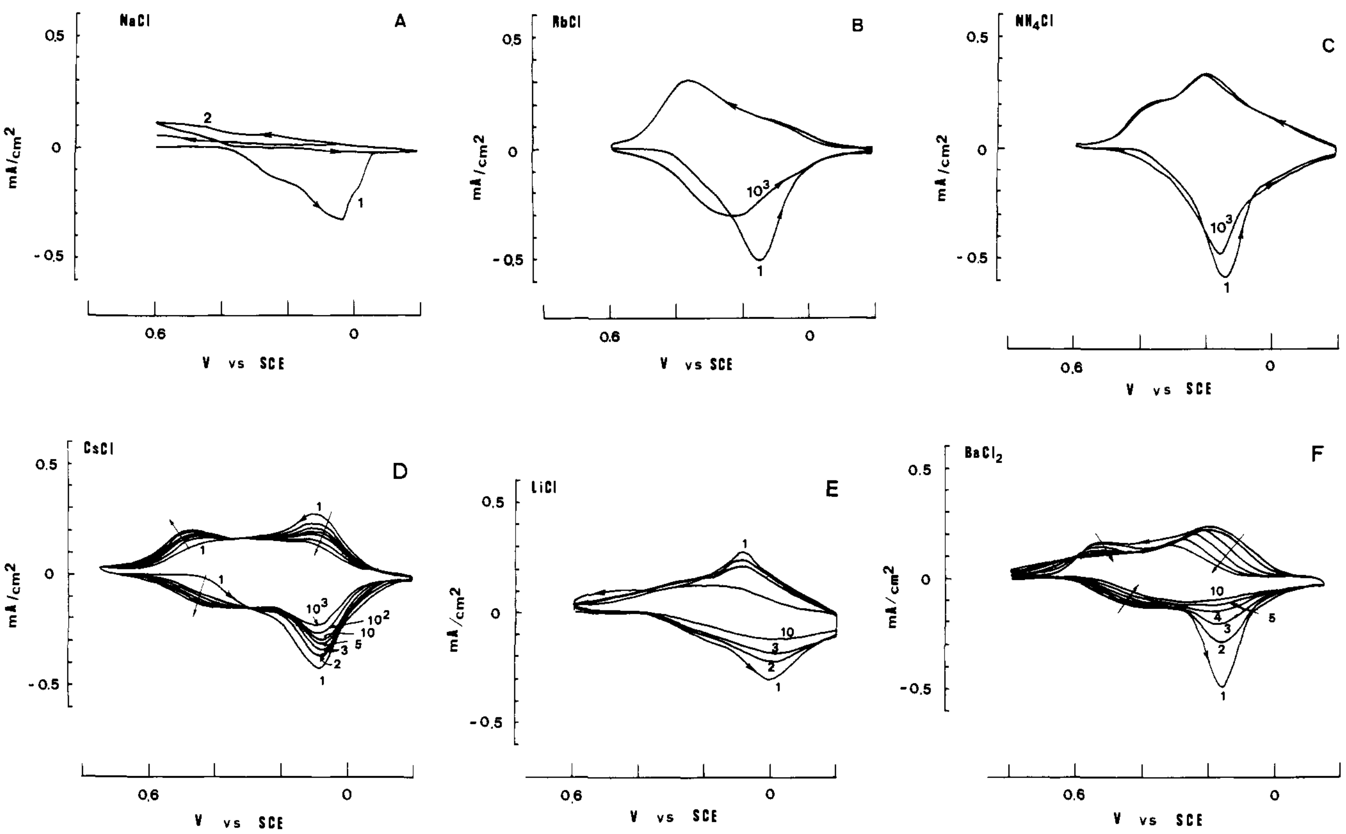

Figure 6. Cyclic voltammograms of PB-modified Pt electrodes with 6 mC/cm² of PB in 0.1 M NaCl (A), 0.1 M RbCl (B), 0.1 M NH_4Cl (C), 0.1 M CsCl (D), 0.1 M LiCl (E), and 0.05 M $BaCl_2$ (F). The scan rate was 20 mV/s. The solutions were purged with pure nitrogen gas. The number in the figure shows the repeated cycle. All pH values of the solutions were adjusted to 4.0.

An atomic absorption spectrometric determination was carried out, which showed only a trace amount of potassium. A typical result was that the concentrations of iron and potassium were respectively 0.8 ppm and less than 0.05 ppm for a PB film deposited at 68.5 mC/cm². The calculated concentrations of iron and potassium are 0.79 and 0.28 ppm for the formula of $KFe^{III}Fe^{II}(CN)_6$ and are 0.7 ppm and zero for $Fe_4{}^{III}[Fe^{II}(CN)_6]_3$, respectively. The above results strongly encourage the view that the formula of the film was not water-soluble PB and was possibly water-insoluble PB.

A coulometric study was performed with a PB-modified SnO_2 electrode in order to obtain a further observation. Figure 4 shows the coulometric behavior of the electrode in 1 M KCl (pH 4.0) as well as a cyclic voltammogram. The voltammogram shown in Figure 4 was recorded after 5–10 repeated scans between 0.6 and −0.2 V. On the scan from 0.6 to −0.2 V, the integrated current of 3.3 mC/cm² was obtained. The coulometric curve came back to almost zero, indicating that no side reaction was involved in the waves at 0.2 V. On the scan from 0.6 to 1.4 V, a fairly large background prevented a precise determination of the charge consumed at the oxidation wave of PB, so the electrode potential was kept at 1.4 V for 10 s and then scanned to a less positive potential. The amount of the total charge consumed at the reduction of the oxidized form of PB was 2.3 mC/cm². The ratio of the charges is 0.7, which shows directly that the formula of PB is water-insoluble PB. As shown in Figure 4, a second anodic peak appeared at about 1.15 V. This is a reversible reaction and the corresponding reduction peak appeared at about the same potential. Exactly the same results were obtained in the solutions of 0.5 M K_2SO_4 (pH 4.0) and of 0.05 M KBF_4.

Figure 5 shows the absorption spectra obtained on the SnO_2 electrode with 10.5 mC/cm² for the amount of PB at the different electrode potentials. At the electrode potential of 0.6 V, the spectrum was assigned to PB with a wavelength of 700 nm at the peak position. The absorbance obtained at 700 nm was 0.857. On the basis of the above values, the molar extinction coefficients were calculated as 7880 and 10 500 $L^2\ mol^{-1}\ cm^{-1}$ with respect to Fe^{III} and $Fe^{II}(CN)_6$, respectively, assuming the formula of $Fe_4{}^{III}[Fe^{II}(CN)_6]_3$. Robin obtained a molar extinction coefficient of 9800 $L^2\ mol^{-1}\ cm^{-1}$ at $14.1 \times 10^3\ cm^{-1}$ by using a colloidal form of PB prepared by adding a stoichiometric amount of $K_4Fe^{II}(CN)_6$ to a $Fe^{III}(ClO_4)_3$ solution.[8] The value of 10 500 with respect to the number of $Fe^{II}(CN)_6$ in the film is almost the same as Robin's value. Three different amounts of PB, 4.7, 8.9, and 17.8 mC/cm², deposited on SnO_2 electrodes gave 0.375, 0.73, and 1.46 for the absorbances at 700 nm. The above measurement shows a perfect straight line with a zero intercept, yielding a value of the slope of 81.5 (±0.5) cm²/C. To our knowledge, the present measurement of the optical extinction of PB represents the first determination of this property since Robin's first experiments gave rather approximate results.

The spectrum obtained at −0.2 V did not show any distinct bands in the visible region. The spectrum obtained at 1.40 V showed a band at 420 nm. However the spectrum obtained at 1.1 V showed bands at 420 cm and about 770 nm. Ellis et al. reported that the absorption at 700 nm persisted in the oxidized form of PB at 1.1 V and about one-third of the ferrocyanide ion remained unoxidized.[12] They concluded that the oxidized form of PB included ferrocyanide ions and a definite formula was $K_{1/3}Fe^{III}[Fe^{II}(CN)_6]_{1/3}\cdot[Fe^{III}(CN)_6]_{2/3}$ for the oxidized form of PB.[12] This conclusion was definitively based on the rather ill-defined spectrum obtained at 1.1 V (see Figure 8 in ref. 12). We noted that the peak position was observed at 770 nm, not 700 nm, in the spectrum obtained at 1.1 V. It is noteworthy that the peak positions of the intervalence charge-transfer band are considerably shifted to longer wavelength for the partially oxidized form of PB and are dependent on the degree of the oxidation. Such a shift of the peak position is also observed for the partially reduced form of PB.[30] However, no appreciable absorption band due to the intervalence charge transfer was found in the spectrum obtained at 1.4 V, as shown in Figure 5. The film at 1.4 V was visually

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(30) Itaya, K.; Uchida, I.; Ataka, T.; Toshima, S.; Ito, O.; Matsuda, M., unpublished result (1982).

brown, no green. These results show that the oxidation of PB is fully carried out electrochemically at 1.4 V vs. SCE. The observed color for the fully oxidized form of PB is extremely important. Although the brown color has long been expected for the fully oxidized form of PB,[4] no one has reported the optical absorption spectrum of this compound. Iron(III) hexacyanoferrate(III) had not hitherto been prepared chemically in the pure state[27] because of its high oxidation power, as demonstrated in Figure 4.

Ellis et al. assigned the band at 420 nm to the $^2T_{1g} \rightarrow {}^2T_{2g}$ ligand–metal charge transfer in the ferricyanide ion.[12] However, we found that this band was quite similar to the spectrum obtained in a solution of ferric ferricyanide reported by Ibers and Davidson.[17] A molar extinction coefficient of 4200 $L^2\ mol^{-1}\ cm^{-1}$ is calculated at 420 nm from data from Figure 5 with respect to the number of $Fe^{III}(CN)_6$ in the film, 0.75×10.5 mC/cm^2. A similar value, about 3000, was reported.[17] This correspondence suggests that the oxidized form of PB, even though it is a crystal form, has a similar situation to a one-to-one complex between Fe^{III} and $Fe^{III}(CN)_6$ in a solution.

Cation Effects on the Wave at 0.2 V. The crystal structure of PB is a face-centered cubic lattice with a cell constant of 10.5 Å,[10] indicating an open structure. PB is zeolitic and acts as a molecular sieve with channel diameters of about 3.2 Å.[4,25] As is formulated in eq 1 and 2, the wave at 0.2 V must involve the penetration of the cations of supporting electrolytes in order to maintain electroneutrality. Ellis et al. have given a description of the cation effects on the wave at 0.2 V.[12] However, the details have not been reported yet.

The electrochemistry of PB was examined in the 0.1 M solutions of HCl, LiCl, NaCl, RbCl, CsCl, NH_4Cl, and tetraethylammonium perchlorate, (TEAP) and in a 0.05 M solution of $BaCl_2$. All pH values of the solutions were adjusted to pH 4.0 by hydrochloric acid, except the solution of TEAP whose pH was adjusted by perchloric acid. Figure 6 shows the cyclic voltammograms obtained from these solutions. An amount of PB (about 6 mC/cm^2) was deposited on a platinum disk electrode at a current density of 10 μA/cm^2, and then about ten repeated scans were taken in a solution of KCl in order to get a steady voltammogram as shown in Figure 1A.

It is obvious that the surface waves at 0.2 V are strongly affected by the cations of the supporting electrolytes. In the case of NaCl, the wave was immediately destroyed after one scan from 0.6 to −0.2 V. No reoxidation wave was observed. It was noticed that the blue film could be seen on the electrode surface even though the voltammogram collapsed as shown in Figure 6A, and sometimes the film departed from the electrode surface. Exactly the same behavior was observed in solutions of TEAP and of HCl.

The voltammograms obtained in solutions of NH_4Cl and of RbCl were very stable, although the waves observed were less symmetric than that in a solution of KCl. In the above case, repeated scans up to 10^3 between 0.6 and −0.2 V caused only less than 5% decrease in the total charge. This suggests that the cations of NH_4^+ and Rb^+ can transport through the open spaces in the crystal of PB.

In the case of CsCl, as shown in Figure 6D, a less stable nature was found, but still the transport of Cs^+ seemed to be possible. About 20% loss in the total charge was observed after 10^3 repeated scans. Much less stable natures were found in solutions of LiCl and $BaCl_2$. About 30% and 60% losses were found in the solutions of LiCl and of $BaCl_2$ after 10 repeated scans, respectively.

The above results can be quantitatively explained by the radii of the hydrated ions. The radii calculated from the limiting mobility by Stokes' law are 2.37, 1.83, 1.25, 1.18, 1.19, 1.25, 2.81, and 2.88 Å for Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, TEA^+, and Ba^{2+}, respectively.[26] Only K^+, Rb^+, Cs^+, and NH_4^+ can be expected to transport through a crystal of PB. The results shown in Figure 6 agree completely with this expectation.

The behavior observed in the films prepared at the higher current density, 100 μA/cm^2, was somewhat different. For example, the wave at 0.2 V persisted for about 10 repeated scans in a solution of NaCl. It could be seen that part of the film gradually disappeared from the electrode surface. This is probably due to the rough surface structure of the PB film prepared at a higher current density, as observed in SEM.

Finally, it must be pointed out that the anions of supporting electrolytes diffuse into or out of the PB crystal in the oxidation of PB at 0.9 V. We have examined the electrochemistry of the PB film in solutions of the potassium salts of BF_4^-, F^-, PF_6^-, SO_4^{2-}, ClO_4^-, and NO_3^-. In the case of BF_4^-, the wave at 0.9 V is extremely stable. The repeated scan between 0.6 and 1.4 V showed only 10% decrease after 10^4 cycles. In the case of PF_6^- and F^-, the reactions were completely blocked, in the same manner as that shown in Figure 6A. The details will be published soon.

Conclusions

The purpose of this study was to describe the electrochemical preparation method and the spectroelectrochemistry of Prussian blue. The film of Prussian blue ($Fe^{III}_4[Fe^{II}(CN)_6]_3$) was almost quantitatively formed by the electrochemical reduction in the ferric ferricyanide solution. K^+, Rb^+, Cs^+, and NH_4^+ could transport through the open spaces in the crystal of Prussian blue. The optical extinctions of Prussian blue, Prussian white, and Berlin green were determined by the spectroelectrochemical method. The fully oxidized form of Prussian blue, $Fe^{III}_4[Fe^{III}(CN)_6]_3$, could be prepared; its spectrum showed only a band at 420 nm. The absorption at 700 nm did not persist in the fully oxidized form.

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Registry No. $Fe_4^{III}[Fe^{II}(CN)_6]_3$, 14038-43-8; $KFe^{III}Fe^{II}(CN)_6$, 25869-98-1.