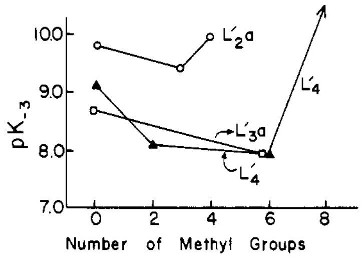

Figure 7. Plot of pK_{-3} vs. the number of α-carbon methyl groups in L for the $Cu^{II}(H_{-3}L)$ or $Cu^{II}(H_{-2}L)(OH)$ complexes. The arrow for the Aib_4 point indicates the lower limit for pK_{-3}.

For the tetrapeptides and the tripeptide amides, deprotonation of the third peptide nitrogen (K_{-3}, eq 18) occurs at 0.7–2

$$Cu(H_{-2}L) \overset{K_{-3}}{\rightleftharpoons} Cu(H_{-3}L) + H^+ \qquad (18)$$

pK_a units lower than loss of the third proton from equatorial coordinated water in the dipeptide amide series as shown in Figure 7. The pK_{-3} value is lowest for the Aib series relative to the glycyl series in accord with the inductive effect of the α-carbon methyl group. For the tetrapeptides, coordination of the third peptide nitrogen is possible only as long as the fourth amino acid residue is not an Aib. The tetrapeptide Aib_4 does not form the $Cu(H_{-3}L)$ species because of steric hindrance to coordination between the rest of the complex and the fourth residue. Structure **3a** is proposed for $Cu^{II}(H_{-2}Aib_4)^-$ rather than a structure similar to **3c** because an equatorially coordinated water molecule would be expected to ionize at pH values below 10.5.

Conclusions

The volume occupied by the α-carbon methyl groups in the Aib residue is an important steric effect that restricts the conformation of peptides containing this residue. This study shows that the Aib units can hinder copper(II) coordination in a few cases. Thus, coordination of the third peptide nitrogen in the Aib_4–copper(II) complex does not occur. A destabilizing effect due to the steric requirements of the α-carbon methyl groups is seen in the formation of the first chelate ring (**1**) and in the formation of the first 5–5–5 fused chelate system (**3a**). However, in general, the copper(II)–peptide complexes containing Aib residues are more stable than the corresponding alanyl or glycyl complexes. The increased stability of the Aib-containing peptide complexes of copper(II) is due largely to the inductive effect of the α-carbon methyl groups. The increase in overall stability varies with the length of the peptide and is largest for the tetrapeptides (with the exception of Aib_4). Thus, $Cu^{II}(H_{-3}Aib_3G)^{2-}$ is ~40 times more stable than $Cu^{II}(H_{-3}G_4)^{2-}$. Overall, the relative stability of the Aib complexes is determined by a balance between enhanced stability due to the inductive effects and destabilization due to the space requirements of the α-carbon methyl groups.

Acknowledgment. This investigation was supported by Public Health Service Grant Nos. GM 19775 and GM 12152 from the National Institute of General Medical Sciences and by a Phillips Petroleum Fellowship (A.W.H.). We are grateful to Brigette Schwederski for the synthesis of the tripeptide GAibG.

Registry No. AAib, 84799-80-4; Aib_2, 39692-70-1; GAibG, 87453-23-4; $AAib_2$, 83917-78-6; Aib_3, 50348-89-5; G_2AibG, 82628-39-5; Aib_3G, 87453-24-5; Aib_4, 50348-91-9; Aiba, 16252-90-7; AAiba, 87453-25-6; Aib_2a, 87453-26-7; Aib_3a, 82628-40-8.

Contribution from the P. M. Gross Chemistry Laboratory, Department of Chemistry, Duke University, Durham, North Carolina 27706, and Research Triangle Institute, Research Triangle Park, North Carolina 27709

Use of a Metal-Containing Plasma Polymer Coating To Prepare a Prussian Blue Surface Modified Electrode

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Graphite electrodes are surface modified by coating them in a glow-discharge plasma chamber with iron pentacarbonyl (the resulting deposit is called an iron-containing plasma deposit) or iron pentacarbonyl and ethane in a 1:1 molar ratio (the resulting deposit is called an iron-containing plasma polymer). Both modified electrodes have surface bound redox-active iron centers that are characterized by cyclic voltammetry. Either of these surface modified electrodes may be further modified by electrochemical reaction with hexacyanoferrate to form surface adherent Berlin green, Prussian blue, and Everitt's salt, which may be interchanged reversibly by changing the potential of the electrode. Well-defined cyclic voltammograms

$$\underset{\text{Berlin green}}{[MFe^{3+}Fe^{II}(CN)_6]_{1/2}[Fe^{3+}Fe^{III}(CN)_6]_{1/2}} \xleftarrow{-^1/_2e^-,\ -^1/_2M^+} \underset{\text{Prussian blue}}{MFe^{3+}Fe^{II}(CN)_6} \xrightarrow{e^-,\ M^+} \underset{\text{Everitt's salt}}{M_2Fe^{2+}Fe^{II}(CN)_6}$$

$$M^+ = K^+, Na^+$$

are obtained in neutral aqueous solution by using the Prussian blue surface modified working electrode. Surface adherence of the Prussian blue persists over several thousand cycles. Concentrations of surface adherent redox-active Prussian blue increase to as high as 2×10^{-7} mol/cm^2 with increased nominal coatings of iron-containing plasma polymer or iron-containing plasma deposit on the graphite electrode surface. The Prussian blue modified electrode is permeable to both K^+ and Na^+ ions, and the kinetics of the oxidation–reduction processes at the electrode surface are controlled by diffusion of the electrolyte cation in and out of the lattice. Experiments with mixed electrolytes in aqueous solution demonstrate a cation preference in the order $K^+ > Na^+ >> Li^+$.

Introduction

Research into modified electrode surfaces, which began only a decade ago, has developed into an active area of current interest.[2] Various techniques have been utilized to modify the surface of an electrode; these include dipping, electrodeposition, covalent attachment, and plasma polymerization of

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[1] (a) Duke University. (b) Research Triangle Institute.

[2] See, for example, the following review articles: (a) Ryan, M. D.; Wilson, G. S. *Anal. Chem.* **1982**, *54*, 20R. (b) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135. (c) Snell, K. D.; Keenan, A. G. *Chem. Soc. Rev.* **1979**, *8*, 259.

0020-1669/83/1322-3541$01.50/0

Table I. Experimental Conditions of Plasma Polymerizations

row	monomer feed	ΣF,[a] cm³/min	F_{Fe},[b] cm³/min	rf power, W	$10^8 W/FM$,[c] J/kg	P_g,[d] mtorr	P_m,[e] mtorr
1	ethane/$Fe(CO)_5$	0.10	0.05	50	60	7	2.4
2	$Fe(CO)_5$	0.10	0.10	50	34	17.6	3.5

[a] Sum of the flow rates ($Fe(CO)_5$ and ethane). [b] $Fe(CO)_5$ flow rate. [c] Energy per unit mass of monomer. [d] Pressure inside the reactor during glow discharge. [e] Pressure inside the reactor prior to glow discharge.

selected monomers. These surface modified electrodes have proven useful as electrocatalysts, in analytical devices, and in the characterization of polymer solutions. For these and other reasons investigations of modified electrode surfaces are of some importance.

Redox-active molecules have been chemically and physically attached to the surface of platinum, gold, and carbon electrodes.[2] In several instances physical modification of the electrode has been carried out by using a polymeric support to coat the surface. This surface adsorbed polymer may contain a Lewis base such as poly(vinylpyridine),[3] which is capable of chemically binding aqueous metal ions and then confining them to the electrode surface. Vinylferrocene has been plasma polymerized on the surface of an electrode to give a surface bound redox-active center.[4,5]

We have examined the electrochemical properties of $Fe(CO)_5$ that has been plasma deposited on a graphite electrode in a glow discharge and of an $Fe(CO)_5$ and ethane combination that has been plasma polymerized in a glow discharge and deposited onto a graphite electrode surface. Both the iron-containing plasma deposit and plasma polymer exhibit a redox-active signal when examined by cyclic voltammetry. An interesting characteristic of our iron/plasma surface modified graphite electrode is that it can react with hexacyanoferrate to form surface adherent Berlin green, Prussian blue, and Everitt's salt, which may be interchanged reversibly by changing the potential of the electrode.

Prussian blue is a mixed-oxidation-state iron cyanide.[6] Characterization by IR,[7] Mössbauer,[8] and optical spectroscopy[9] confirms formulation as iron(III) hexacyanoferrate(II). Two forms of Prussian blue have been dubbed as "soluble", $KFeFe(CN)_6$, and "insoluble", $Fe_4[Fe(CN)_6]_3$, although both are highly insoluble in water.[6,10] Prussian blue is known to undergo a one-electron oxidation to give Berlin green (ferric ferricyanide) and a one-electron reduction to yield Everitt's salt (ferrous ferrocyanide). Recenty, several reports have appeared in the literature describing the electrochemistry of surface bound Prussian blue. These investigations utilize Prussian blue surface modified electrodes prepared by chemical[11-13] or electrochemical[13-17] deposition on a platinum, gold, or glassy carbon[16] substrate. A membrane/paste electrode incorporating Prussian blue has also been investigated.[18]

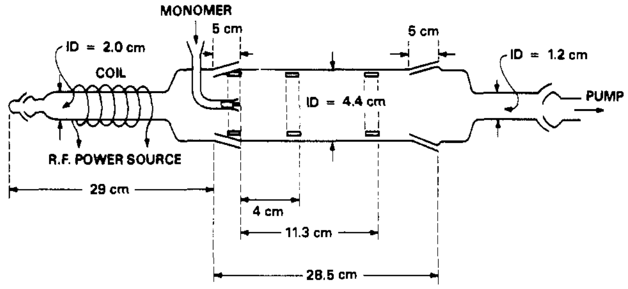

Figure 1. Schematic representation of plasma reactor.

The Prussian blue surface modified electrode described in this report differs significantly from that of previous reports in its method of preparation on a graphite electrode surface modified in a $Fe(CO)_5$ or $Fe(CO)_5$/ethane plasma, the ease and reproducibility of each electrode preparation, the well-defined nature of cyclic voltammogram peaks, the tenacity of surface adherence in neutral aqueous medium, and the permeability to both potassium and sodium ions.

Experimental Section

Materials. Ethane was obtained from Airco Inc. and used without purification. Iron pentacarbonyl was obtained from Aldrich Chemical Co., stored as received at −78 °C, and warmed to 0 °C during plasma polymerizations. Sodium and potassium hexacyanoferrate were obtained from Pfaltz and Bauer and Fisher, respectively. Lithium, sodium, and potassium nitrate, were obtained from Fisher and recrystallized from water/acetone (85%/15%) prior to use. Water used in cyclic voltammetry measurements was purified by distilling conductivity water from acidic $K_2Cr_2O_7$ and then slowly from basic $KMnO_4$ in an all-glass apparatus with Teflon sleeves and stopcocks. Carbon rods (0.3 cm × 3.8 cm) used for plasma polymer deposition and cyclic voltammetric measurements were obtained from Ultracarbon (Ultra F purity) and extracted with hot CH_3CN for 18 h prior to use.

Methods. Plasma polymerizations were carried out in the inductively coupled cylindrical reactor previously described[19] with a modified (2 mm i.d.) orifice for monomer introduction; 50 W of rf power (13.56 MHz) was used. (See Figure 1). Table I contains a listing of the important variables controlled for each plasma polymerization. Carbon rods were mounted along the reactor axis at a distance of 0.5 cm from the monomer inlet for direct deposition of the metalated polymer. Nominal plasma polymer (or deposit) film thickness on the carbon rod was calculated from gravimetric data obtained by placing an aluminum strip in the reactor the same distance (in projection) from the monomer orifice as the carbon rod.

Cyclic voltammetry was performed by using a Bioanalytical Systems CV-1B triangular wave generator, a Ag/AgCl reference, a Pt auxiliary, and a plasma polymer surface-modified working electrode. Cyclic voltammograms were recorded on a Houston Instruments Model 100 *x–y* recorder. The potential measured midway between the cathodic and anodic peak currents (i_{pc}, i_{pa}) is referred to as E_{av} and is reported relative to the Ag/AgCl reference electrode. In all experiments 0.54 cm² of the working electrode surface was exposed to the electrolyte solution. Two types of cell configurations were used. The most frequent was a one-cell three-electrode (plasma polymer surface modified working electrode; Ag/AgCl reference electrode; Pt auxiliary electrode) system. In a two-cell three-electrode configuration the

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(3) See, for example: Shigehara, K.; Oyama, N.; Anson, F. C. *J. Am. Chem. Soc.* **1981**, *103*, 2552.

(4) See, for example: (a) Umana, M.; Denisevich, P.; Rolinson, D. R.; Nakahama, S.; Murray, R. W. *Anal. Chem.* **1981**, *53*, 1170. (b) Umana, M.; Rolison, D. R.; Nowak, R.; Daum, P.; Murray, R. W. *Surf. Sci.* **1980**, *101*, 295.

(5) See, for example: Dautartas, M. F.; Mann, K. R.; Evans, J. F. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *110*, 379.

(6) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(7) Wilde, R. E.; Ghosh, S. N.; Marshall, B. J. *Inorg. Chem.* **1970**, *9*, 2512.

(8) Ito, A.; Suenaya, M.; Ono, K. *J. Chem. Phys.* **1968**, *48*, 3597.

(9) Robin, M. B. *Inorg. Chem.* **1962**, *1*, 337.

(10) Ludi, A.; Güdel, H. U. *Struct. Bonding (Berlin)* **1973**, *14*, 1.

(11) Neff, V. D. *J. Electrochem. Soc.* **1978**, *125*, 886.

(12) Ellis, D.; Eckhoff, M.; Neff, V. D. *J. Phys. Chem.* **1981**, *85*, 1225.

(13) Kellawi, H.; Rosseinsky, D. R. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *131*, 373.

(14) Itaya, K.; Ataka, T.; Toshima, S. *J. Am. Chem. Soc.* **1982**, *104*, 4767.

(15) Itaya, K.; Shibayama, K.; Akahoshi, H.; Toshima, S. *J. Appl. Phys.* **1982**, *53*, 804.

(16) Itaya, K.; Akahoshi, H.; Toshima, S. *J. Electrochem. Soc.* **1982**, *129*, 1498.

(17) Itaya, K.; Ataka, T.; Toshima, S.; Shinohara, T. *J. Phys. Chem.* **1982**, *86*, 2415.

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

(19) Yasuda, H.; Lamaze, C. E. *J. Appl. Polym. Sci.* **1973**, *17*, 1519.

auxiliary electrode was placed in the second cell connected by an agar–salt bridge. Scrubbed nitrogen (chromous solution) was bubbled through the electrolyte solutions prior to making the cyclic voltammetric measurements, which were performed in a nitrogen atmosphere. Electrode surface coverage of the electroactive species was calculated by integration of the area encompassed by the current–voltage plots.

Analysis for iron leached from plasma polymer or plasma deposit into the electrolyte solution was performed by graphite furnace atomic absorption spectrometry. An Instrumentation Laboratories Model 357, equipped with a Model 655 graphite furnace and Model 254 autosampler, was used. Analysis was performed at the 248.3-nm line with deuterium arc background correction. The instrument was calibrated with aqueous standards prepared from a commercially available 1000 ppm stock solution diluted with 0.5% nitric acid. The detection limit was 0.15 ppb.

Results and Discussion

Plasma Polymer Film Preparation. Graphite electrodes were coated in a glow discharge using an iron pentacarbonyl monomer (the resulting deposit will be called an iron-containing plasma deposit) or iron pentacarbonyl and ethane in a 1:1 molar ratio (the resulting deposit will be called an iron-containing plasma polymer).[20] The conditions used to prepare the plasma polymers and plasma deposits investigated are given in Table I. The important preparative variables under our control are monomer ratio (hydrocarbon/$Fe(CO)_5$), power to flow rate ratio (W/FM), pressure, and plasma polymer or deposit film thickness. Flow rates are used to control the monomer ratio, and both flow rates and reaction time determine the plasma polymer or deposit film thickness. The naked graphite and plasma polymer coated electrode surfaces were investigated by using scanning electron microscopy and found to be extremely rough. For this reason it is not possible to determine the actual thickness of the plasma polymer (or deposit) electrode coating. However, a nominal loading may be calculated (based on the assumption that the surface is smooth) and regulated by controlling the exposure time to the plasma.

Characterization of these metalated plasma polymer surfaces on various substrates by Mössbauer, IR, and ESCA spectroscopic techniques is the subject of subsequent publications.[20,21] These results may be summarized briefly as follows. Mössbauer spectra obtained for electrodes coated at the conditions of row 1 and row 2 (Table I) are consistent with a single iron component, high-spin iron(III). FTIR spectra were obtained for plasma polymer (and deposit) films deposited on an aluminum foil substrate. Films prepared at row I (Table I) conditions exhibit spectra consistent with the presence of iron carboxylate and iron oxide. ESCA spectra are consistent with the formation of films containing iron oxide utilizing the oxygen from $Fe(CO)_5$.

To summarize, the plasma polymer coatings of rough-surfaced graphite electrodes are deposits of unknown thickness and uniformity that contain iron oxide and iron carboxylate in a cross-linked hydrocarbon plasma polymer matrix. Those preparations made with both $Fe(CO)_5$ and ethane as comonomers are designated as iron-containing plasma polymers. Films prepared at the conditions of row 2 in Table I in the absence of ethane comonomer are called iron-containing plasma deposits. The exact structure and composition of the plasma polymer and plasma deposit film coatings are not completely understood, but its effects are entirely reproducible.

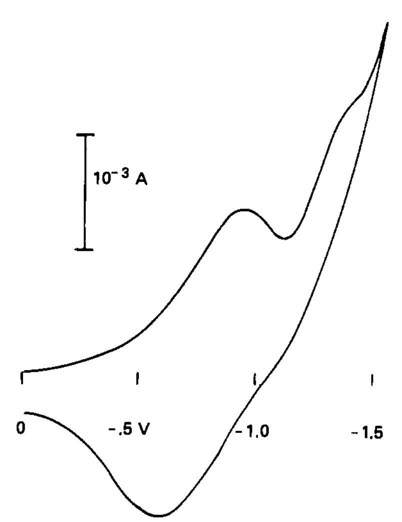

Figure 2. Cyclic voltammogram obtained in aqueous solution (0.1 M KNO_3) by using an iron-containing plasma polymer surface modified working electrode prepared at the conditions described in row 1, Table I (nominal thickness 10 μg/cm², scan rate 100 mV s^{-1}). Similar cyclic voltammograms were obtained by using working electrodes prepared at row 2 conditions found in Table I.

Electrochemistry of Plasma Polymer Coated Electrodes. Cyclic voltammograms were obtained in aqueous solution (0.1 M KNO_3) by using an iron-containing plasma polymer or plasma deposit coated on a carbon rod working electrode at the conditions shown in Table I. A cathodic peak was observed at −1.0 V and an anodic peak at −0.55 V (Figure 2), consistent with the presence of an oxide of iron (see above).[22,23] The presence of the latter peak is dependent upon cycling through the −1.0 V peak. When a hydrocarbon plasma polymer film is deposited on the electrode surface in the absence of $Fe(CO)_5$, the signals at −1.0 and −0.55 V are not present, thus confirming our assignment of these peaks to redox involving iron on the electrode surface.

Signal intensities decrease with repeated cyclic scans either over the entire solvent window or the negative-potential region. Only weak peak current signals are evident after 100 cyclic scans. Signal intensity was also found to decrease on a longer time scale when a constant potential was maintained at 0 V for approximately 2 h. However, analysis of the electrolyte solution after being held at 0 V for 140 min and cycled 20 times (0–1.2 V) with use of atomic absorption spectroscopy shows only a 0.2% loss of iron from the iron-containing plasma polymer electrode coating (row 1, Table I).[24] On the other hand, as much as 25% of the iron is lost from the iron-containing plasma deposit coated electrode (row 2, Table I) after similar treatment.

Electrochemistry in the Presence of Hexacyanoferrate. The iron-containing plasma polymers and plasma deposits on graphite electrodes were tested for their permeability or conductivity with respect to electroactive species in solution. Graphite working electrodes coated with an iron-containing plasma polymer or plasma deposit were cycled from −0.2 to +0.6 V in an aqueous solution containing 0.005 M $K_3Fe(CN)_6$ and 0.1 M KNO_3. The voltammograms showed the expected

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(20) Morosoff, N.; Patel, D. L.; Lugg, P. S.; Crumbliss, A. L. *J. Appl. Polym. Sci.: Appl. Polym. Symp.*, in press.

(21) Morosoff, N.; Patel, D. L.; White, A. R.; Brown, D. B.; Umana, M.; Lugg, P. S.; Crumbliss, A. L., submitted for publication in *Thin Solid Films*.

(22) These redox signals are reproducible but only present when the electrode is plasma coated directly in front of the monomer inlet (Figure 1). This condition was met for all electrode preparations reported here.

(23) Suzuki, I.; Hisamatsu, Y.; Masuko, N. *J. Electrochem. Soc.* **1980**, *127*, 2211. Okada, H.; Hosoi, Y.; Naito, H. *Corrosion (Houston)* **1970**, *26*, 429.

(24) The concentration of iron detected in the solution was more than 10 times the detection limit of the method. The mass of iron in the electrode coating was estimated from the known deposition rate of iron-containing plasma polymer in the preparation of the coating (and duration of exposure to the plasma), the nominal surface area (of the graphite electrode) exposed to the electrolyte solution, and the weight percent of iron in the coating (as obtained both by atomic emission spectroscopy of nitric acid digested iron-containing plasma polymer and by ESCA).[21]

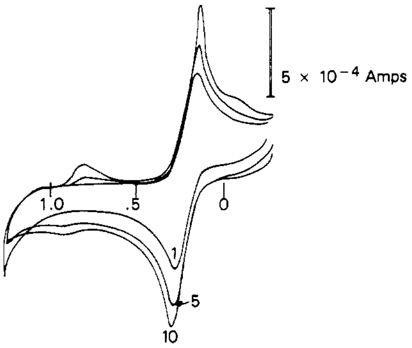

Figure 3. First, fifth, and tenth cyclic voltammograms obtained in a 0.005 M $K_3Fe(CN)_6$ and 0.1 M KNO_3 aqueous solution by using an iron-containing plasma polymer surface modified (row 1, Table I; nominal thickness 10 $\mu g/cm^2$) working electrode (scan rate 100 mV s^{-1}).

strong redox couple for $Fe(CN)_6^{3-/4-}$ at $E_{av} = 0.23$ V. This suggests either that hexacyanoferrate can diffuse through the polymer film to the electrode surface or that the coating is discontinuous. When the scan range for the cyclic voltammograms was −0.2 to +1.2 V, a second weak couple appeared at $E_{av} = 0.89$ V (see Figure 3). Repeated cycling increased the intensities of both couples at 0.89 and 0.21 V. When electrodes treated in this way were removed from the aqueous hexacyanoferrate solution, rinsed, and then cycled in an aqueous KNO_3 solution in the absence of hexacyanoferrate, both redox couples continued to be observed.[25]

These observations are in contrast to an untreated graphite electrode or one coated with an ethane plasma polymer containing no iron, which when cycled did not exhibit a second couple at $E_{av} \sim 0.9$ V that increased in intensity with cycling. Neither did it produce a surface adherent redox-active species. When the naked graphite or hydrocarbon plasma polymer coated electrode was removed from the aqueous hexacyanoferrate solution, rinsed, and placed in a fresh aqueous KNO_3 solution, there were no observable redox signals other than those associated with water decomposition.

Evidence eliminating the possibility that the presence of a surface adherent redox-active hexacyanoferrate species is a result of an electrode surface modification brought about by the presence of CO or O_2 in the glow discharge was also obtained. Graphite electrodes were independently exposed to a CO or O_2 plasma at power and flow rate conditions similar to those used in the plasma polymerization reactions. In each case the graphite electrode was then held at 0 V in a 0.005 M $K_3Fe(CN)_6$ solution for 140 min and cycled in a 0.1 M KNO_3 solution that did not contain hexacyanoferrate (optimum conditions for redox-active hexacyanoferrate deposition; see below). In neither case was there any evidence of an electrode surface adherent redox-active species. These results eliminate the possibility that oxygen, which may be produced from $Fe(CO)_5$ in our plasma polymerization reactions, attacks the graphite surface to produce hexacyanoiron attachment sites (e.g., by carboxylate functional group formation).[26]

The E_{av} values observed (Figure 3) are in good agreement with values reported[11-17] for the oxidation (~0.9 V) and reduction (~0.2 V) of Prussian blue films deposited on electrodes by electrochemical or chemical methods. Also, IR and UV–vis spectroscopic analyses of the modified electrode surface using photothermal detection methods demonstrate surface adherent redox-active Prussian blue.[27] Consequently, our observations are consistent with the formation of Prussian blue on the surface of a carbon electrode coated with an iron-containing plasma polymer or plasma deposit film when cycled in hexacyanoferrate solution over the range from −0.2 to 1.2 V. Furthermore, the Prussian blue remains surface bound when the electrode is removed from the aqueous hexacyanoferrate solution. The surface bound Prussian blue can be oxidized and reduced over several cycles according to Scheme I.

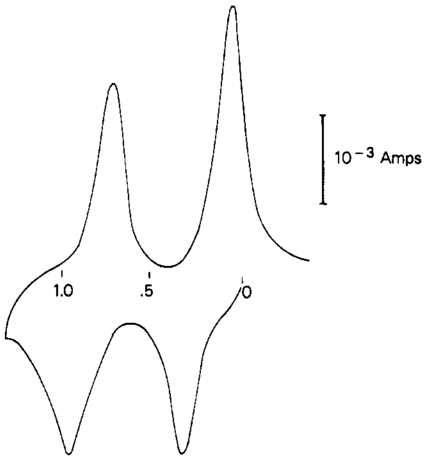

Figure 4. Cyclic voltammogram obtained in aqueous 0.1 M KNO_3 by using an iron-containing plasma polymer surface modified (row 1, Table I; nominal thickness 10 $\mu g/cm^2$) working electrode after it has been prepared by being held for 140 min at 0 V in an aqueous solution containing 0.005 M $K_3Fe(CN)_6$ and 0.1 M KNO_3 and then removed and rinsed (scan rate 100 mV s^{-1}).

Scheme I

$$\text{Berlin green} \overset{+0.89\text{ V}}{\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}} \text{Prussian blue} \overset{+0.21\text{ V}}{\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}} \text{Everitt's salt}$$

Prussian blue is a mixed-valence species with high-spin iron(III) and low-spin iron(II) and is formulated as ferric ferrocyanide.[6,10] In situ Mössbauer measurements[17] have conclusively shown that the reduction of Prussian blue to Everitt's salt (or Prussian white) proceeds via the reduction of high-spin iron(III) to iron(II). The oxidation of Prussian blue gives a compound commonly called Berlin green or Prussian green, which is formally ferric ferricyanide. The exact stoichiometry of Berlin green is uncertain, but there does appear to be some consensus that complete oxidation of ferrocyanide does not occur. Prussian blue occurs in two forms, "soluble" and "insoluble", both of which are highly insoluble in water.[6,10] Evidence supporting the formation of the soluble form of Prussian blue and the approximate stoichiometry for Berlin green in our system will be presented below.

Prussian Blue Adherence on Plasma Polymer Coated Electrodes. The rate of surface adherent Prussian blue formation on either the iron-containing plasma polymer or plasma deposit surface modified electrode is greatly enhanced by keeping the potential of the working electrode in an aqueous 0.005 M $K_3Fe(CN)_6$ solution (0.1 M KNO_3) at 0 V for 140 min with constant stirring. As noted above, an insignificant amount of iron from the iron-containing plasma polymer leaches into the solution at these conditions. Figure 4 illustrates a cyclic voltammogram for an iron-containing plasma polymer surface modified electrode that has been pretreated in this way, rinsed with distilled water, and then cycled in an aqueous 0.1 M KNO_3 solution that does not contain hexacyanoferrate. The presence of two redox couples with E_{av} at 0.89 and 0.21 V

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(25) It should be noted that iron-containing plasma polymer or plasma deposit coated graphite electrodes did not exhibit any redox signals due to surface bound species when simply soaked in aqueous $K_3Fe(CN)_6$ or $K_4Fe(CN)_6$, rinsed, and then cycled in aqueous KNO_3.

(26) Miller, C. W.; Karweik, D. H.; Kuwana, T. *Anal. Chem.* **1981**, *53*, 2319.

(27) Childers, J. W.; Crumbliss, A. L.; Lugg, P. S.; Palmer, R. A.; Morosoff, N.; Patel, D. L. *J. Phys.* (*Orsay, Fr.*), in press.

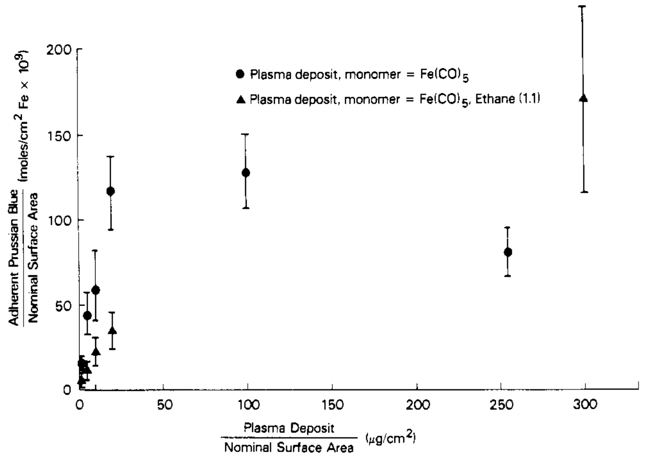

Figure 5. Plot of the amount of adherent Prussian blue vs. nominal thickness of plasma polymer coating when the plasma polymer coated electrode is preconditioned by treatment in an aqueous solution containing 0.1 M KNO_3 and 0.005 M $K_3Fe(CN)_6$ at 0 V for 140 min. The amount of adherent Prussian blue is obtained from the area under the cyclic voltammogram peak centered at 0.2 V. Error-bar limits were obtained from separate measurements using the cathodic and anodic portions of the cyclic voltammogram peak centered at 0.2 V: (▲) iron-containing plasma polymer coated electrode prepared at row 1, Table I conditions; (●) iron-containing plasma deposit coated electrode prepared at row 2, Table I conditions.

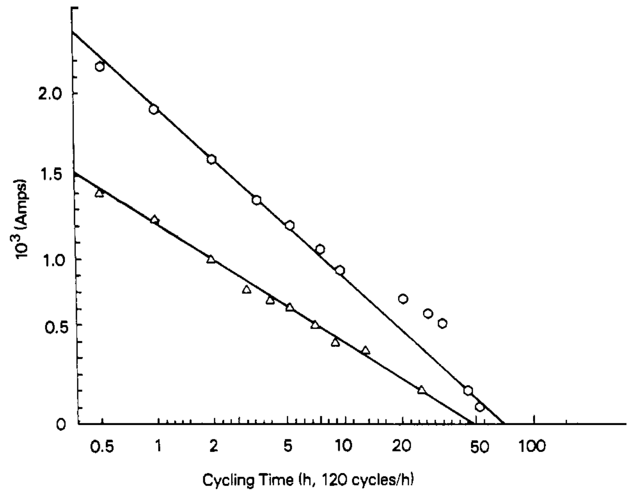

Figure 6. Plot of cathodic peak current for E_{av} centered at 0.2 V as a function of the logarithm of the cycling time: (△) iron-containing plasma polymer surface modified electrode (row 1, Table I; 10 $\mu g/cm^2$ nominal thickness); (○) iron-containing plasma deposit surface modified electrode (row 2, Table I; 10 $\mu g/cm^2$ nominal thickness). Both electrodes were preconditioned by treatment in an aqueous solution containing 0.1 M KNO_3 and 0.005 M $K_3Fe(CN)_6$ at 0 V for 140 min followed by rinsing and then cycling in 0.1 M aqueous KNO_3.

demonstrates the presence of surface adherent redox-active Prussian blue. The intensity and persistence of these redox couples show this to be an efficient technique for producing a Prussian blue surface modified electrode. A similar cyclic voltammogram may be obtained in aqueous KNO_3 solution by pretreating an iron-containing plasma deposit surface modified working electrode (row 2, Table I) in the same way.

The influence of plasma polymer nominal loading on the intensity of the redox peaks resulting from surface adherent Prussian blue was determined in the following way. Graphite electrodes were coated with iron-containing plasma polymer films with nominal loadings of 1, 5, 10, 20, and 300 $\mu g/cm^2$. Each electrode was held in a 0.005 M $K_3Fe(CN)_6$ solution for 140 min at 0 V. The electrodes were then rinsed and cycled in 0.1 M aqueous KNO_3. The redox signal at E_{av} = 0.21 V was integrated, and a plot of the surface adherent concentration of electroactive species as a function of plasma polymer film nominal thickness was made. These data are shown in Figure 5 and demonstrate that as the quantity of iron-containing plasma polymer coating increases, the concentration of surface adherent hexacyanoferrate is also increased. Figure 5 also illustrates the observed increase in surface bound redox-active Prussian blue with an increase in surface coating for iron plasma deposits (row 2, Table I) for nominal loadings of 5, 10, 20, 100, and 254 $\mu g/cm^2$. Electrode pretreatment was carried out as described above.

A quantitative measure of the durability of the Prussian blue bound to the iron-containing plasma polymer and plasma deposit coated electrodes was obtained as follows. Two electrodes coated with 10 $\mu g/cm^2$ nominal loading of either iron-containing plasma polymer or iron-containing plasma deposit were treated in aqueous $K_3Fe(CN)_6$ for 140 min at 0 V, rinsed, and then cycled from −0.2 to +1.2 V in aqueous KNO_3 (0.1 M). A plot of cathodic peak current for E_{av} = 0.21 V as a function of the logarithm of the number of cycles is shown in Figure 6 for both electrode surfaces. This plot shows that Prussian blue will adhere to either electrode surface for 5000 or more cycles. It may be noted that the rate of decay is higher for Prussian blue adherent to the iron-containing plasma deposit than for that adherent to the iron-containing plasma polymer. This may be due either to the higher loading of Prussian blue deposit on the iron-containing plasma deposit (see Figure 6) or to an intrinsic characteristic of the iron-containing plasma deposit vis-à-vis the iron-containing plasma polymer.

It is probable that decomposition of hexacyanoferrate at the auxiliary electrode plays a key role in forming Prussian blue at the working electrode surface during the pretreatment process, that is, when the working electrode is held at 0 V in a 0.005 M $K_3Fe(CN)_6$ solution. This is supported by three observations. Firstly, at the conditions described the auxiliary electrode obtains a potential greater than 1.6 V. Secondly, when the auxiliary electrode is isolated from the working electrode solution containing hexacyanoferrate by an agar–salt bridge, Prussian blue is not deposited on the working electrode surface when its potential is maintained at 0 V for 140 min. Thirdly, $K_3Fe(CN)_6$ may be oxidized at a platinum working electrode maintained at 1.65 V for 140 min with a two-cell three-electrode configuration. When an iron-containing plasma polymer treated electrode is subsequently soaked in this oxidized solution (no current flowing), rinsed, and then cycled in a fresh 0.1 M KNO_3 solution (containing no hexacyanoferrate), redox coupes at E_{av} = 0.88 and 0.19 V appear. This is consistent with an iron hexacyanoferrate species being formed at the Pt working electrode, which then coats the iron-containing plasma polymer (or deposit) surface modified electrode on soaking.[25,28]

The mechanism for surface attachment of Prussian blue to the iron-containing plasma polymer or plasma deposit coated electrode is somewhat speculative at this time. However, experimental evidence suggests that Prussian blue, including its oxidized and reduced forms, is attached at the working electrode surface through the iron sites of the plasma polymer (or deposit) film. This anchoring most probably occurs through a cyanide bridge and precludes physical entrapment of Prussian blue in the pores of the graphite or the ethane plasma polymer matrix. This model is based on the following experimental observations: (1) Hexacyanoferrate will not

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(28) While the presence of these cyclic voltammetry signals at E_{av} = 0.88 and 0.19 V does confirm the presence of surface adherent Prussian blue, repeated cycling in 0.1 M KNO_3 brings about the rapid disappearance of these signals.

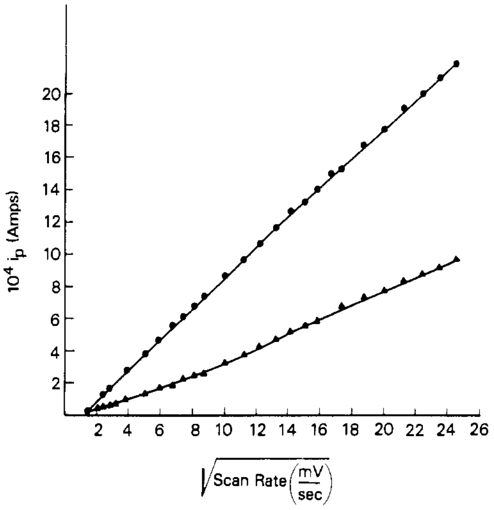

Figure 7. Plot of cathodic peak current vs. square root of the scan rate for cyclic voltammograms obtained in 0.1 M KNO_3 by using iron-containing plasma deposit (row 2, Table I; nominal thickness 10 $\mu g/cm^2$) surface modified electrode pretreated by holding at 0 V for 140 min in an aqueous solution containing 0.005 M $K_3Fe(CN)_6$ and 0.1 M KNO_3 and then removed and rinsed with distilled water. Similar plots were obtained by using an iron-containing plasma polymer (row 1, Table I) surface modified electrode: (▲) cathodic peak current associated with E_{av} = 0.89 V; (●) cathodic peak current associated with E_{av} = 0.21 V.

adhere to a naked graphite electrode, an ethane plasma polymer modified graphite (no iron) electrode, or graphite electrodes that have been exposed to a CO or O_2 plasma when these electrodes are cycled in 0.005 M $K_3Fe(CN)_6$.[29] (2) Cycling an iron-containing plasma polymer or plasma deposit coated electrode in an aqueous $K_3Fe(CN)_6$ solution results in the immediate appearance of redox couples at E_{av} = 0.89 and 0.21 V. (3) An increase in the nominal loading of the iron-containing plasma polymer or plasma deposit coating on the working electrode surface results in an increase in concentration of surface bound Prussian blue, presumably because of an increase in plasma polymer bound iron attachment sites on the electrode surface.

Preliminary attempts to prepare a redox-active surface adherent Prussian blue electrode by coating a smooth-surfaced platinum electrode with 0.5 $\mu g/cm^2$ of the iron-containing plasma polymer were not completely successful. No redox peaks are initially observed on scanning from 0 to 1.2 V in an aqueous solution containing 0.005 M $K_3Fe(CN)_6$ and 0.1 M KNO_3. A peak is observed at E_{av} = 0.21 V after repeated scans. This peak persists on rinsing and removal to a solution containing only KNO_3 electrolyte; however, the full Prussian blue signature is not observed. The results obtained with the rough-surfaced graphite electrode must therefore require either a coating of less than 0.5 $\mu g/cm^2$ actual loading or a discontinuous coating.

Role of the Electrolyte Cation. A graph of peak current for E_{av} = 0.89 and 0.21 V plotted as a function of scan rate for the iron-containing plasma deposit (row 2, Table I) modified electrode with surface adherent Prussian blue cycled in aqueous KNO_3 (0.1 M) is shown in Figure 7. A similar plot is obtained by using an iron-containing plasma polymer (row 1, Table I) coated electrode. This figure illustrates that the peak current for both redox couples is directly proportional to the square root of the scan rate. The separation between cathodic and anodic peak currents for the high-spin and low-spin redox couple was found to decrease from 325 to 40 mV as the scan rate was decreased from 500 to 2 mV s^{-1}. These results are the same, regardless of whether the cations of the bulk solvent are K^+ or Na^+ (see below).

Monolayers of surface adsorbed redox-active species typically have peak currents that are directly proportional to the scan rates. Diffusion control of the redox process from ions in the bulk solution yields a square root dependence of the peak current on scan rate.[30] The results shown in Figure 7 are consistent with the diffusion of K^+ ion in and out of the lattice of surface bound Prussian blue upon reduction or oxidation. This process is represented in Scheme II and suggests that the surface adherent Prussian blue contains K^+ ions in the interstices and therefore may be closely related to what is called the soluble form of Prussian blue, $KFeFe(CN)_6$. Further support for this conclusion comes from the fact that E_{av} for Prussian blue oxidation depends on the identity of the alkali metal cation in solution (see below). This is in contrast to the work of Itaya and co-workers,[14,16] whose electrode preparation produced the insoluble form of Prussian blue, which when oxidized was dependent upon anion diffusion into the lattice for charge balance. Experiments performed with chloride salts as electrolytes produced no change in the observed E_{av} values, thus demonstrating that there are no specific anion effects in our system.

Direct integration of the *i–V* curves permit an interpretation of the stoichiometries involved in the redox process as shown in Scheme II. Integration of the cathodic peaks at 0.9 and 0.2 V gives a value of Q for the reduction of Berlin green which is one-half that obtained for the reduction of Prussian blue (n = 0.5 ± 0.06). Thus, the oxidation of Prussian blue to Berlin green is incomplete. Neff and co-workers[12] have also noted this and hypothesize that the open polymeric network of completely oxidized Berlin green is unstable and requires some K^+ in the lattice for stability. The electrochemical formation of Berlin green with the stoichiometry $[KFe^{3+}Fe^{II}(CN)_6]_{1/3}[Fe^{3+}Fe^{III}(CN)_6]_{2/3}$ reported by Neff[12] is qualitatively consistent with our results, which are summarized in Scheme II.

Scheme II

$$\underset{\text{Berlin green}}{[MFe^{3+}Fe^{II}(CN)_6]_{1/2}[Fe^{3+}Fe^{III}(CN)_6]_{1/2}} \xleftarrow{-{}^1/_2e^-,\ -{}^1/_2M^+}$$

$$\underset{\text{Prussian blue}}{MFe^{3+}Fe^{II}(CN)_6} \xrightarrow{e^-,\ M^+} \underset{\text{Everitt's salt}}{M_2Fe^{2+}Fe^{II}(CN)_6}$$

$$M = K^+,\ Na^+$$

Electrode preparations may be carried out in the presence of Na^+ ions instead of K^+ ions using both the iron-containing plasma polymer and plasma deposit surface modified electrodes with essentially the same results. For these experiments, electrode pretreatment was carried out with $Na_3Fe(CN)_6$ and $NaNO_3$. For example, an iron-containing plasma deposit treated electrode was held at 0 V for 140 min in an aqueous solution containing $NaNO_3$ and $Na_3Fe(CN)_6$ (0.1 and 0.005 M, respectively). This electrode was then rinsed and cycled in aqueous 0.1 M $NaNO_3$. Two sets of redox couples were observed at E_{av} = +1.05 and 0 V (see Figure 8). Submerging this electrode in an aqueous 0.1 M KNO_3 solution gave a cyclic voltammogram with peak currents at potentials typical of those of the electrode prepared from the potassium salt of hexacyanoferrate when cycled in aqueous KNO_3, as seen in Figure

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[29] A very light coating of iron hexacyanoferrate may be formed on a naked graphite electrode when soaked overnight in a 0.005 M $K_3Fe(CN)_6$ solution that has been oxidized at a Pt working electrode (1.65 V) as described above. However, the signals at E_{av} = 0.88 and 0.19 V rapidly disappear after cycling the electrode a few times in aqueous 0.1 M KNO_3 in the absence of hexacyanoferrate.

[30] Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980.

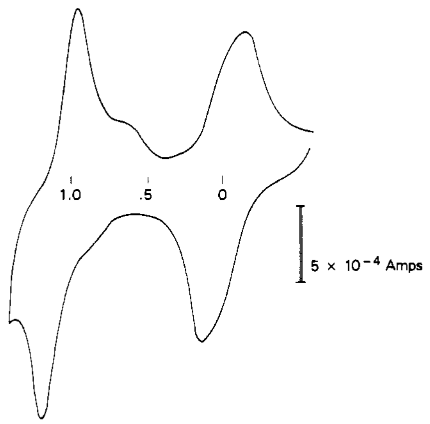

Figure 8. Cyclic voltammogram obtained in aqueous 0.1 M $NaNO_3$ by using an iron-containing plasma deposit surface modified (row 2, Table I; nominal thickness 10 $\mu g/cm^2$) working electrode after it has been maintained for 140 min at 0 V in an aqueous solution containing 0.005 M $Na_3Fe(CN)_6$ and 0.1 M $NaNO_3$ and then removed and rinsed (scan rate 100 mV s^{-1}).

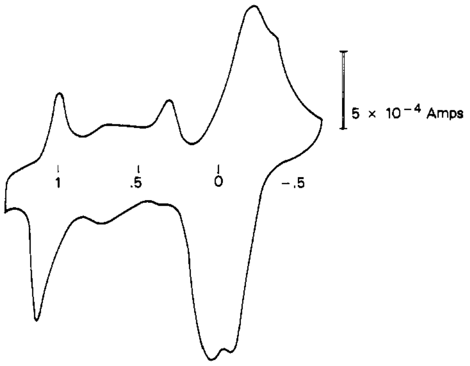

Figure 9. Cyclic voltammogram obtained in aqueous 0.1 M $NaNO_3$ by using the working electrode from Figure 4 after it was removed from aqueous KNO_3 solution and placed in 0.1 M $NaNO_3$ solution for 15 min at 1.2 V (scan rate 100 mV s^{-1}).

4. The reverse of this procedure produces a more complex cyclic voltammogram. An iron-containing plasma polymer coated electrode pretreated at 0 V for 140 min in a 0.005 M solution of $K_3Fe(CN)_6$ containing 0.1 M KNO_3 exhibits an initially complex cyclic voltammogram when rinsed and cycled in 0.1 M $NaNO_3$. Peak currents shift during the initial cycles (scan rate 100 mV/s), but after 10 min of cycling from −0.55 to +1.15 V, there is no change in signal intensity. A representative cyclic voltammogram is shown in Figure 9 where E_{av} = 1.05 and 0 V.

The use of $LiNO_3$ as the bulk electrolyte in these same experiments gives poorly resolved redox couples on the first scan, which quickly disappear after the second scan. This is true whether the surface coating is either an iron-containing plasma polymer or plasma deposit and whether the surface adherent Prussian blue is originally formed from KNO_3 or $NaNO_3$ electrolyte solution. For example, when a Na^+ containing Prussian blue surface modified electrode is cycled in an aqueous 0.1 M $LiNO_3$ solution, a total loss of both redox signals is observed after 20 cycles over the range from −0.2 to +1.2 V. Returning this electrode to $NaNO_3$ restores only ca. 5% of the original peak current signals after more than 20 cycles. An electrode modified with K^+ containing Prussian blue gives similar results.

These results demonstrate that the cations of the bulk electrolyte have a substantial effect on the iron hexacyanoferrate E_{av} values and i–V peak shapes. These effects can readily be seen by comparing Figures 4 and 8. Structural information available for the potassium salt of the soluble form of Prussian blue[6,10,31] shows a repeating cubic lattice with potassium counterions occupying the center of alternate cubes. Therefore, the potassium cations must diffuse in and out of the lattice when Prussian blue is reduced or oxidized. This cation diffusion is the current limiting factor in our cyclic voltammetry experiments when the scan rate is rapid, as discussed above and shown in Figure 7. This cation diffusion in and out of the lattice must be responsible for the ready replacement of Na^+ for K^+, and vice versa. The zeolitic nature of Prussian blue has been noted previously.[32]

The use of mixed electrolytes in obtaining cyclic voltammograms of surface adherent Prussian blue suggests that there is a definite preference for K^+ diffusion in and out of the lattice. An iron-containing plasma polymer film coated electrode, treated as described above by using $K_3Fe(CN)_6$ in 0.1 M KNO_3, when rinsed and placed in a mixed electrolyte solution (0.05 M KNO_3, 0.05 M $NaNO_3$) exhibits a i–V curve characteristic of that observed in KNO_3 solution (K^+ signature) and not a mixture of the two. A similar observation (K^+ signature in mixed electrolyte) was made when the electrode was prepared by using $Na_3Fe(CN)_6$ in $NaNO_3$ electrolyte solution. Likewise, when an electrode with surface adherent Prussian blue is placed in a mixed electrolyte solution containing either KNO_3 (0.05 M) and $LiNO_3$ (0.05 M) or $NaNO_3$ (0.05 M) and $LiNO_3$ (0.05 M), the cyclic voltammogram obtained is identical with that obtained in KNO_3 and $NaNO_3$ electrolyte solutions, respectively. Significantly, there is no deterioration of the i–V signal in either case after repeated cycling as is observed in $LiNO_3$ electrolyte solution. These results suggest that both K^+ and Na^+ can successfully compete with Li^+ for the surface adherent redox-active Prussian blue lattice.

Since the cyclic voltammogram signal disappears when the electrode is cycled in aqueous $LiNO_3$, either Li^+ is unable to diffuse into the Prussian blue lattice or once incorporated it cannot diffuse out. Two consequences of the greater charge/radius ratio of Li^+ (relative to Na^+ or K^+) that may be responsible for this observation are (i) an enhanced electrostatic force of attraction that may hinder Li^+ diffusion out of the lattice and (ii) a larger hydration radius[33] that may retard Li^+ diffusion into the lattice. Results obtained in nonaqueous medium[34] suggest that both effects may be operative.

Summary and Conclusions

(1) A graphite electrode that has been surface modified by the deposition of an iron-containing plasma polymer film or iron-containing plasma deposit film is capable of being further electrochemically modified by the adherence of redox-active Prussian blue.

(2) It is suggested that the effect of the iron-containing plasma polymer or plasma deposit is to provide insoluble iron sites on the electrode surface for attachment of Prussian blue components generated in solution. Other effects of the plasma such as CO or O_2 plasma activation of the graphite surface were eliminated as possible causes. The effect of adding a hydrocarbon to the monomer mixture is to bind the high-spin iron(III) (iron oxide and carboxylate) more effectively to the graphite electrode, with no effect on the nature of binding to Prussian blue.

(3) Well-defined cyclic voltammograms may be obtained in neutral aqueous solution containing 0.1 M $NaNO_3$ and/or KNO_3 using a Prussian blue surface modified working electrode.

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(4) Surface coverage by the Prussian blue can be as high as 2×10^{-7} mol/cm^2 and will tenaciously adhere for several thousand oxidation–reduction cycles over the entire redox-active potential range from 0 to +1.2 V in neutral aqueous medium.

(5) Experimental evidence suggests that it is the soluble form of Prussian blue, $KFeFe(CN)_6$, that adheres to the electrode, presumably through cyanide bridges to the iron sites on the plasma polymer (or deposit) surface modified electrode.

(6) Further evidence was presented to show that Prussian blue may be reduced to form Everitt's salt, $M_2Fe^{2+}Fe^{II}(CN)_6$, and partially oxidized to Berlin green, $M_{1/2}Fe^{3+}(Fe^{III}(CN)_6)_{1/2}(Fe^{II}(CN)_6)_{1/2}$ ($M = K^+, Na^+$).

(7) The kinetics of these oxidation–reduction processes at the electrode surface are controlled by diffusion of the electrolyte cation in and out of the Prussian blue lattice.

(8) Both K^+ and Na^+ migrate in and out of the film and produce well-defined cyclic voltammograms whose E_{av} values are alkali metal cation dependent. Cyclic voltammograms obtained in mixed electrolytic solutions establish the following order of cation selectivity in aqueous medium: $K^+ > Na^+ >> Li^+$.

The method of surface preparation and several key features (e.g., points 3, 5, 7, and 8) of the Prussian blue adherent surface modified graphite electrode reported here are different from those in recent reports in the literature where polymeric Prussian blue is deposited on a electrode by chemical precipitation[12] or electroplating.[14] Itaya and co-workers present evidence to suggest that in their case the insoluble form of Prussian blue is attached to the electrode surface.[14] The permeability of the film to both Na^+ and K^+ ions is in contrast to previous workers who have investigated the redox behavior of Prussian blue films deposited on other substrates by different means and who report no activity in the presence of Na^+.[12,14]

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Registry No. $Fe(CO)_5$, 13463-40-6; $K_3Fe(CN)_6$, 13746-66-2; $KFe^{3+}(Fe(CN)_6)$, 25869-98-1; $Na_3Fe(CN)_6$, 14217-21-1; $K_2Fe^{2+}(Fe(CN)_6)$, 15362-86-4; $K_{1/2}Fe^{3+}(Fe^{III}(CN)_6)_{1/2}(Fe^{II}(CN)_6)_{1/2}$, 87371-33-3; K, 7440-09-7; Na, 7440-23-5; graphite, 7782-42-5; ethane, 74-84-0.

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Simultaneous Conversion of Ni-PR_3 and B-H to Ni-H and B-PR_3 Linkages by Thermal Rearrangement of d^8 *closo*-Bis(triarylphosphine)nickelacarboranes. Crystal and Molecular Structure of [*closo*-3-(μ-CO)-8-PPh_3-3,1,2-$NiC_2B_9H_{10}$]$_2$: A Dimeric Nickelacarborane Complex Containing a Metal-Metal Bond

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The reaction of L_2NiCl_2 ($L = PR_3$) species with *nido*-7,8-, *nido*-7,9-, or *nido*-2,9-$C_2B_9H_{11}^{2-}$ ions led to the formation of the corresponding icosahedral bis(phosphine)nickelacarboranes in high yield. Heating members of the *closo*-3,3-(triarylphosphine)$_2$-3,1,2-$NiC_2B_9H_{11}$ series at 80 °C in benzene solution led to the formation of the corresponding [*closo*-3,8-(triarylphosphine)$_2$-3-H-3,1,2-$NiC_2B_9H_{11}$] by interchange of phosphine and hydrido ligands. No intermediates were observed, and the reaction was specific for the bis(triarylphosphine)–3,1,2-NiC_2 icosahedral system among those investigated. The dimeric nickelacarborane carbonyl [*closo*-(3-(μ-CO)-8-PPh_3-3,1,2-$NiC_2B_9H_{11}$)$_2$] was prepared by a variety of routes such as the reaction of [*closo*-3,3-(PPh_3)$_2$-3,1,2-$NiC_2B_9H_{11}$] (**1a**) with CO in benzene at 80 °C. A variety of ligand substitution reactions were carried out with **1a**. The mechanism of the phosphine–hydride ligand interchange is discussed. The dimeric nickelacarborane complex was characterized by an X-ray diffraction study. Amber crystals were triclinic, space group $P\bar{1}$, with $a = 13.319$ (4) Å, $b = 10.039$ (3) Å, $c = 9.813$ (3) Å, $\alpha = 80.00$ (1)°, $\beta = 82.91$ (1)°, $\gamma = 110.32$ (1)°, and $Z = 1$. The structure was solved by conventional heavy-atom methods to a final discrepancy index of $R = 0.057$ for 2233 independent observed reflections. The complex contains a metal–metal bond (2.477 (2) Å) and two metal–bridging carbon monoxide groups.

We have previously reported the formation of the *closo*-hydridonickelacarborane complex **1b** through an unusually facile thermolysis of the *closo*-bis(triphenylphosphine)nickelacarborane complex **1a**.[1] The reaction involved the interchange of a nickel-bound phosphine with the hydrogen atom of an adjacent boron vertex of the dicarbollide ligand, thereby forming B–P and Ni–H bonds, respectively (Figure 1). This type of ligand-interchange reaction has also been demonstrated with (phosphine)rhodacarborane[2] and (phosphine)ruthenacarborane[3] complexes in these laboratories and with (phosphine)platinacarborane[4] complexes elsewhere. In an attempt to establish the possible mechanism and scope of these reactions, a series of *closo*-bis(phosphine)nickelacarboranes was prepared and characterized (Figure 2).

Results and Discussion

Reaction of the respective *nido*-7,8-, *nido*-7,9-, or *nido*-2,9-$C_2B_9H_{11}^{2-}$ ions[5] with the appropriate bis(phosphine)nickel dihalide in dichloromethane (Tl_2 salt) or tetrahydrofuran (Na_2 salt) afforded the bis(phosphine)nickelacarborane complexes **1–6**, **9**, and **10** in high yield. Of the bis(phosphine)nickela-

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