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SPECTRAL CHARACTERIZATION OF REDOX-ACTIVE PRUSSIAN BLUE ON METALLATED PLASMA POLYMER SURFACE MODIFIED CARBON ELECTRODES USING PHOTOTHERMAL DETECTION


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Abstract - Electro-generated Prussian blue, Berlin green, and Everitt's salt bound to the surface of iron-containing plasma polymer-coated graphite electrodes have been characterized by visible and FT-IR PTS (PAS). The results are compared to those obtained by diffuse reflectance.

I. INTRODUCTION

Optical spectroscopic characterization of surface-bound species on highly absorbing, irregularly shaped, massive substrates presents a problem well suited to photothermal spectroscopy (PTS), using either conventional sample-gas-microphone or photothermal deflection techniques. Some IR results on such samples have appeared in the literature (1), although work with powdered substrates has been more common (2,3). In the case of finely divided materials, particularly when absorptivity is low or dilution with a transparent powder is possible, diffuse reflection spectroscopy (DRS) has been shown to be a competitive, or even superior technique (4). However, when, in addition to high absorptivity, the sample has the relatively low surface area and high specular reflectivity of a massive, irregular object (as in the case of the work reported here), the advantages of PTS over DRS are more clearly apparent. In this paper we present photothermal spectra in the visible, NIR and IR of Prussian blue and related hexacyanoferrates on carbon electrode rods surface-modified by deposition of a metallated plasma polymer or plasma deposit film. In situ spectral characterization of these species bound on carbon electrode surfaces has not previously been reported, although their spectra in powders and thin films has been well established by other techniques (5,6).

II. ELECTRODE PREPARATION AND PROPERTIES

Metal-containing plasma polymers may be prepared by exposing a volatile metal carbonyl and a hydrocarbon to a glow discharge (7). The product deposited in a similar process using only the volatile metal carbonyl is referred to as a plasma deposit. The carbon rod electrodes studied in this work were first surface-modified by a coating of such a plasma deposit (or plasma polymer) made from Fe(CO)_5 (and ethane), using 50 W of rf power (13.56 MHz). Nominal loadings of 10-300 µg cm^-2 are typical, although the roughness of the surface observed by scanning electron microscopy indicates that the actual surface coverage is much lower. The quantity and characteristics of plasma polymer deposited depend on the flow rate and mixing ratio of the gases, the pressure of the plasma, the length of deposition time, the plasma chamber geometry and the position of the substrate relative to the gas inlet, as well as the rf power used. The
metallated plasma polymer film used in this investigation is thought to contain iron(III) carboxylates and iron(III) oxide in a highly crosslinked matrix. Evidence for this comes from Mossbauer and ESCA spectra, as well as FT-IR ATR spectra of films deposited on aluminum foil. The plasma polymer film has also been characterized by cyclic voltammetry (8).

Iron-containing plasma polymer or plasma deposit surface-modified electrodes may be further surface-modified to produce electrodes with surface adherent, redox active Prussian blue by exposing the electrode to cyclic voltammetry in an aqueous solution 0.1 M in KNO₃ and 0.005 M in K₃[Fe(CN)₆], cycling from -0.2 V to +1.2 V (Ag/AgCl). This binding may also be affected by maintaining the electrode at a potential of 0 V in the above solution for a period of time, with stirring (8). A cyclic voltammogram typical of Prussian blue is obtained, with ΔEₚ values of 0.89 and 0.21 V, in addition to the oxidation and reduction waves of the polymer-bound iron at -1.0 and -0.55 V, respectively. This voltammogram is unaffected by water rinsing or by transfer of the electrode into an aqueous KNO₃ solution containing no hexacyanoferrate. The electrode can undergo several thousand oxidation-reduction cycles in aqueous solution. A model for the surface adherence which is consistent with the available data is that the new electroactive material consists of crystallites of Prussian blue bound through peripheral ligands to vacant coordination sites on the plasma polymer-bound iron atoms (8).

Since the structure of Prussian blue (5) involves a three dimensional network of -Fe(II)-C=N-Fe(III)-N=C=N- bonds, this implies that the crystallites are bound to the polymer iron(III) ions via cyanide nitrogen atoms (figure 1). Except for these points of attachment, the structure should be expected to exhibit the properties of pure crystalline Prussian blue. Likewise, the reduced and oxidized species indicated by the cyclic voltammograms should be essentially pure Everitt's salt and Berlin green, respectively. Integration of the voltammograms (figure 2) indicates the following electrochemistry:

\[ [KFe^{3+}Fe^{II}(CN)_6]_2[Fe^{3+}Fe^{III}(CN)_6]_2 \rightarrow KFe^{3+}Fe^{II}(CN)_6 \rightarrow K_2Fe^{2+}Fe^{III}(CN)_6 \]

Berlin green \hspace{1cm} Prussian blue \hspace{1cm} Everitt's salt

The three surface adherent species can be selectively produced at nominal coverages of up to \(2 \times 10^{-4}\) mole cm \(^{-2}\) by holding the electrochemical potential at +0.9 to +0.2 V (Prussian blue), > +0.9 V (Berlin green) or < +0.2 V (Everitt's salt) for a suitable time.

Although Prussian blue surface adherent electrodes have been prepared by other methods (9,10), our technique results in several key features which are unique; namely, that (i) well defined cyclic voltammograms of surface-bound Prussian blue may be obtained in neutral aqueous solution containing NaNO₃ or KNO₃ electrolyte and in propylene carbonate containing NaNO₃, KNO₃ or LiNO₃ electrolyte, (ii) it is the "soluble" form of Prussian blue, KFe[Fe(CN)₆], that adheres to the electrode, (iii) the kinetics of the oxidation-reduction processes at the electrode surface are controlled by diffusion of the electrolyte cation in and out of the Prussian blue lattice, and (iv) the Prussian blue lattice exhibits an order of cation selectivity: \(K^+ > Na^+ >> Li^+\) (8).

Data concerning the nature of the surface-bound redox active hexacyanoferrates which are independent of electrochemical techniques are highly desirable. PTS represents an optimum technique for in situ observation of the carbon electrode surface-bound species. Specific problems to be addressed initially by PTS include: (i) spectroscopic confirmation that the electrode surface-bound iron cyanide is correctly formulated as Prussian blue, which can be reversibly oxidized to Berlin green and reduced to Everitt's salt, and (ii) determination of the influence of ageing and repeated redox cycling on the surface-bound species.

III. PHOTOTHERMAL SPECTRA OF SURFACE-BOUND HEXACYANOFERRATES

Electrodes for spectral investigation were cut from 3 mm rods to appropriate length (ca. 7 mm), surface-modified with metallated plasma polymer and then further loaded with
The redox-active iron hexacyanoferrate as indicated above. Electrodes were rinsed with water, dried in vacuo and transferred under dry \(\text{N}_2\) into the PTS cell. Subsequent transfers between PTS and electrochemical cells were also routinely carried out under nitrogen, although brief exposure to air, even of the reduced species, had no noticeable effect. Prussian blue and Berlin green powders used for comparison data were freshly prepared by standard procedures. Samples of \(K_3\text{Fe(CN)}_6\) and \(K_4\text{Fe(CN)}_6\) were Fisher reagent grade used without further purification.

Visible-NIR PT spectra were obtained on a PAR Model 6001 Photoacoustic Spectrometer with 6002 cell, quartz window, helium transfer gas and modified sample holder. The source modulation frequency was 100 Hz and the resolution, 8 cm\(^{-1}\) (vis) and 32 cm\(^{-1}\) (NIR) (2 mm slits). Carbon black (Norit-A decolorizing charcoal) was used as reference. As many as 10 scans at 100 nm/min were required for suitable S/N, depending on the surface loading.

Infrared PT spectra (600-4000 cm\(^{-1}\)) were recorded on a IBM Model 9195 FT-IR spectrometer with \(\text{N}_2\) purge, germanium film on KBr beamsplitter and globar source. A PAR 6003 PTS accessory was used, with modified sample holder, KBr window and helium transfer gas. The mirror velocity of 0.059 cm/sec (0.235 cm/sec optical velocity) produced modulation frequencies of 141-940 Hz between 500 and 4000 cm\(^{-1}\). A resolution of 8 cm\(^{-1}\) was used. The reference was carbon black (Norit-A). Typically several thousand scans were required for adequate S/N, depending on surface loading. The signal was processed using the standard program of the IBM-9195, which involves Happ-Genzel apodization of the interferogram.

Infra-red DRS data were measured on the IBM-9195 using a Herrick Scientific Model DRA-2CN DRS accessory and LN\(_2\)-cooled MCT detector. The reference was powdered KCl. Adequate S/N could be obtained with a few hundred scans at a mirror velocity of 0.396 cm/sec. Although routine visible-NIR DRS of \(\text{MgO-diluted}\) powders of the pure Prussian blue and Berlin green were obtained using previously described apparatus (11), \textit{in situ} visible-NIR DRS of the electrode-bound species was completely uninformative due to saturation and specular reflectance effects.

\textit{In situ} visible-NIR PTS of the three hexacyanoferrate species obtained sequentially on the same electrode are shown in figure 3. The lack of intervalence CT band in the spectrum of Everitt's salt is consistent with its formulation as the completely reduced \(\text{Fe(II)}\text{Fe(2+)}\) form. The intervalence CT bands in Prussian blue and Berlin green are only slightly different consistent with the formulation of Berlin green as only a partially oxidized form. The green color is seen to arise from the shift of the visible minimum from ca. 25000 cm\(^{-1}\) to ca. 20000 cm\(^{-1}\), consistent with previous reports (6). The FT-IR PTS of the surface bound hexacyanoferrates along with the spectrum of the plasma modified (blank) electrode are shown in figure 4. It is notable that the blank electrode spectrum shows only minor absorptions due to residual water at 3500 cm\(^{-1}\) and 1400 cm\(^{-1}\) and what are presumed to be iron carboxylates in the 1400-1500 cm\(^{-1}\) region. Significantly, no bands due to CO are observed in the blank electrode spectrum.

Clearly the most important feature in the FT-IR data is the CN stretching band in the 2100 cm\(^{-1}\) region. At the 8 cm\(^{-1}\) resolution of these spectra the CN bands of Prussian blue and Everitt's salt are virtually indistinguishable, with a maximum at 2078 cm\(^{-1}\) when freshly prepared. The maximum shifts to 2086 cm\(^{-1}\) on ageing or repeated redox cycling. The CN stretching band of Berlin green is distinctively split with a more intense maximum at 2086 cm\(^{-1}\) and a weaker one at 2170 cm\(^{-1}\). The spectra shown in figure 4a-c were obtained on the same electrode (in the order presented) by returning the electrode to the electrochemical cell for the appropriate time at the desired potential, with subsequent rinsing, drying, etc. From integration of the area under the cyclic voltammogram peaks a nominal loading of \(2 \times 10^{-7}\) mole cm\(^{-2}\) \([\text{FeFe(CN)}_6]\text{H}^+\) was calculated. The weak band at ca. 1400 cm\(^{-1}\) which appears in figure 4b-c is thought to be due to residual \(\text{N}_2\) from the electrolyte.

The coincidence of the Prussian blue and Everitt's salt CN stretch and the splitting of the band in Berlin green are consistent both with the conventional formulations of these species (5) and with the partial nature of the oxidation involved in the formation of...
Berlin green. In Prussian blue, low-spin Fe(II) is bound to the carbon of the CN bridge and high-spin Fe(3+) to the nitrogen, as expected from the relative ligand field strengths of the C and N donor sites. Reduction to Everitt's salt, the Fe(2+)-Fe(II) species, involves changing the oxidation state only of the nitrogen bound iron, which is relatively weakly involved in metal-CNπ* bonding. However, oxidation to Berlin green involves the strong π-back bonding carbon end of the bridge, and this causes a pronounced increase in the CN stretching frequency as the number of electrons available on the iron is decreased. The fact that the new band has ~1/2 the intensity of the band at 2086 cm⁻¹ is consistent with the voltammetric integration, which indicates that Berlin green is only ca. 50% oxidized to the Fe(III)-Fe(3+) form.

The changes in the surface-bound hexacyanoferrates which occur with time are indicated in figures 5 and 6, which show, respectively, the auto-reduction of Berlin green revealed by the disappearance of the 2170 cm⁻¹ CN stretch, and the slow, as yet unidentified, ageing process that occurs in Prussian blue on the electrode surface. Although the redox activity of the surface-bound hexacyanoferrates linearly decreases to zero after thousands of cycles (8), it has previously been thought that this was due to slow removal of the species from the surface. These spectral data suggest that structural changes may also be involved.

The sensitivity of the PTS technique as applied here is difficult to assess since the exact nature of the distribution of the metallated plasma deposit or polymer on the rough surface of the electrode is not known, nor is the exact nature of the aggregation of the cyanoferate species known. Integration of the cyclic voltammograms indicates that for the spectra shown in figures 3 and 4 the loading was 2 x 10⁻¹⁹ mole/cm² of [FeFe(CN)₆]⁺. Considering the dimensions of the Prussian blue cubic lattice (5), this loading translates to ca. 1800 atomic layers of crystalline hexacyanoferrate. The CN stretching band of the surface-bound species was easily detected for nominal loadings of one tenth this value. Improvements to the cell and use of lower mirror velocity should provide another order of magnitude increase in sensitivity. Thus, the potential detection limit can be estimated at ca. 10 atomic layers nominal coverage. What this means in terms of actual hexacyanoferrate crystallite size is still unclear since the microscopic area of the electrode surface as revealed by SEM (8) is at least an order of magnitude greater than that indicated by its gross dimensions, and on the other hand, it seems likely that the polymer, and thus the hexacyanoferrate, is not distributed evenly over the surface.

Efforts to obtain in situ IR spectra of surface-bound hexacyanoferrates by DRS techniques are illustrated in figure 7. Although the presence of CN is clearly indicated and the sensitivity is basically much higher than that of the PTS technique, the strong specular component in the data renders them difficult to interpret at best. FT-IR DRS data on pure powders of Prussian blue and Berlin green showed gross saturation effects in addition to specular complications. FT-IR PTS data on pure powders, by contrast, gave clean, virtually saturation-free spectra. Comparable data via DRS could only be obtained by diluting the pure materials 1:10 with KCl.

IV. SUMMARY

The most important conclusion to be drawn from the PTS results is that the redox-active species on the electrode have been independently identified as Prussian blue, Berlin green and Everitt's salt. Photothermal detection has allowed molecular spectroscopy (both electronic and vibrational) of the surface-bound products of the redox reactions to be observed in situ, non-destructively, so that their identification is unambiguous. Furthermore, although the sensitivity of the PTS technique is less than that of the DRS method, the absorption-spectra quality of the PTS results in contrast with the saturated and specular reflectivity distorted DRS data make PTS a clear choice for molecular surface spectroscopy on this sort of highly absorbing, massive, irregularly shaped sample. The surface PTS data are entirely consistent with previously reported reflectance and absorption of the iron cyanoferrates in powders and thin films and can be used to monitor decomposition and other as yet unidentified subtle changes which occur on ageing of the surface-bound species on the carbon electrodes. Additional spectral investigation of these electrodes including studies of the effect of different alkali cations,
the stability of Berlin green and Everitt's salt and the nature of the plasma polymer are in progress.

V. REFERENCES


Figure 1. Schematic model for binding of hexacyanoferrates to plasma polymer modified carbon electrode.

Figure 2. Cyclic voltamogram of surface-bound hexacyanoferrates in KNO₃ electrolyte.

Figure 3. Visible-NIR PTS of surface-bound hexacyanoferrates. Electrode modified in KNO₃-K₃Fe( CN)₆:
A. at +0.4V (Prussian blue)
B. at +1.1V (Berlin green)
C. at -0.1V (Everitt's salt)
Figure 5. PTS showing autodecomposition of Berlin green on carbon electrode.

Figure 4. FT-IR PTS of surface-bound hexacyanoferrates.
A. plasma deposit coated carbon electrode.
Electrode modified in KNO$_3$-K$_3$Fe(CN)$_6$ electrolyte at:
B. at -0.1V (Everitt's salt)
C. at +0.4V (Prussian blue)
D. at +1.1V (Berlin green)

Figure 6. PTS showing ageing of Prussian blue on carbon electrode.

Figure 7. DRS of Prussian blue on carbon electrode.