

# Infrared Spectroelectrochemical Analysis of Adsorbed Hexacyanoferrate Species Formed during Potential Cycling in the Ferrocyanide/Ferricyanide Redox Couple

Christine M. Pharr<sup>†</sup> and Peter R. Griffiths\*

Department of Chemistry, University of Idaho, Moscow, Idaho 83843

**External reflection FT-IR techniques allowed for in situ examination of interfacial electrochemical events occurring in a thin-layer spectroelectrochemical cell. The formation of an adsorbed hexacyanoferrate (HCF) species on a platinum electrode during potential cycling in the ferri-/ferrocyanide redox couple was investigated. At neutral pH with KCl as electrolyte, a hexacyanoferrate complex forms during potential cycling in the ferri-/ferrocyanide redox couple, but only if the potential limits are quite large. Characterization of the adsorbed complex indicates that it initially adsorbs as soluble Prussian Blue ( $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ ) with no evidence of the presence of insoluble Prussian Blue [ $\text{Fe}_4^{\text{III}}(\text{Fe}_2^{\text{II}}(\text{CN})_6]$ ). This HCF complex can reversibly adsorb and grow on the electrode surface and desorb and decompose to reform solution-phase ferricyanide and ferrocyanide. Adsorption of the HCF complex decreases, but does not completely inhibit, electron transfer.**

The ferricyanide/ferrocyanide redox couple has been extensively studied and characterized by both electrochemical and spectroscopic techniques. This seemingly simple quasi-reversible redox system is therefore often used for characterization of new electrode materials and processes. For Fourier transform infrared (FT-IR) spectroscopic measurements, ferro-/ferricyanide is also excellent for characterization purposes, since the  $\text{C}\equiv\text{N}$  stretching modes of the two members of the redox couple have relatively large absorptivities, producing bands that are well separated in wavenumber and easy to detect. Despite its extensive use, the kinetics of this system are not well understood and are highly dependent upon the characteristics of both the redox solution and the electrode preparation.<sup>1–4</sup>

Numerous authors have noted variations in the electron transfer rate constant,  $k^0$ , as a function of the cation of the electrolyte.<sup>1,5</sup> Peter et al.<sup>6</sup> reported that, in experiments with alkali metal chloride electrolytes,  $k^0$  decreased in the order  $\text{Cs}^+ \approx \text{K}^+ > \text{Na}^+ > \text{Li}^+$ , suggesting that the cations of the electrolyte facilitate the electron-transfer process. McCreery has reported that, in KCl

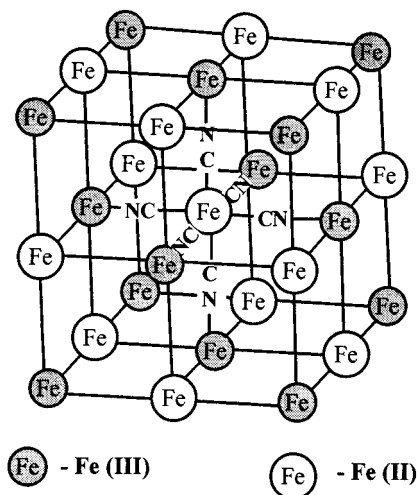


Figure 1. Typical hexacyanoferrate complex in which ferrous and ferric ions are coordinated through cyanide ligands. The lines between iron ions represent the cyanide ligands.

electrolyte, the rate constant for ferrocyanide oxidation decreases with time in solution unless cyanide ions are present.<sup>3</sup> Kinetic measurements by Kawiak et al. indicated an increasing irreversibility of this redox system with successive potential cycling.<sup>7</sup> While the role of the ions in solution is clearly significant, at least in some cases, changes in  $k^0$  have been attributed to an unidentified adsorbate. Several authors suggested that Prussian Blue, an insoluble polymeric hexacyanoferrate (HCF) complex, shown schematically in Figure 1, is adsorbing onto the electrode surface.<sup>3,8</sup> Other authors have presented evidence that ferricyanide and ferrocyanide themselves adsorb onto the electrode surface,<sup>8,9</sup> although Christiansen<sup>10</sup> and Niwa<sup>11</sup> found no evidence of adsorbed species in their experiments.

Evidence is increasing that ferrocyanide and/or ferricyanide adsorb onto the electrode surface;<sup>9,12,13</sup> however, the growth of a HCF complex from solution ferro-/ferricyanide and the experi-

(7) Kawiak J.; Jedral, T.; Galus, Z. *J. Electroanal. Chem.* **1983**, *145*, 163.

(8) Kunimatsu, K.; Shigematsu, Y.; Uosaki, K.; Kitz, H. *J. Electroanal. Chem.* **1989**, *262*, 195.

(9) Wieckowski, A.; Szklarczyk M. *J. Electroanal. Chem.* **1982**, *142*, 157.

(10) Christensen, P.; Hamnett, A.; Trevellick P. *J. Electroanal. Chem.* **1988**, *242*, 23.

(11) Niwa, K.; Doblhofer, K. *Electrochim. Acta* **1986**, *31*, 439.

(12) Fleishman, M.; Graves, P.; Robinson, J. *J. Electroanal. Chem.* **1985**, *182*, 87.

(13) Pharr, C. M.; Griffiths, P. R. *Anal. Chem.* **1997**, *69*, 4665 (preceding paper in this issue).

<sup>†</sup> Present address: Department of Chemistry, Lewis-Clark State College, Lewiston, ID 83501.

(1) Kuta, J.; Yeager, E. *J. Electroanal. Chem.* **1975**, *59*, 110.

(2) Goldstein, E.; Van DeMark M. *Electroanal. Chem.* **1975**, *59*, 110.

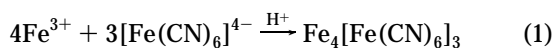
(3) Huang, W.; McCreery R. *J. Electroanal. Chem.* **1992**, *326*, 1.

(4) Kulesa, P.; Jedral, T.; Galus, Z. *J. Electroanal. Chem.* **1980**, *109*, 141.

(5) Goldstein, E. L.; Van De Mark, M. R. *Electrochim. Acta* **1982**, *27*, 1079.

(6) Peter, L.; Durr, W.; Bindra, P.; Gerischer, H. *J. Electroanal. Chem.* **1976**, *71*, 31.

mental conditions associated with its development appear to be in question. HCF complexes are often deliberately synthesized and studied due to interest in their electrochromic properties and possible use for batteries and corrosion inhibition.<sup>14</sup> In such investigations, the HCF complexes are usually adsorbed on electrode surfaces by chemically or electrochemically synthesizing Prussian Blue as shown in eq 1. In this reaction, ferric ions



combine with ferrocyanide to form the insoluble HCF, in which alternating Fe(II) and Fe(III) ions are connected by cyanide ligands. The same product is also formed from the reaction of ferrous ion and ferricyanide, although it is often called Turnbull's Blue rather than Prussian Blue. (Mossbauer spectroscopy has shown synthesis by both methods produces identical structures.<sup>15</sup>) Potential cycling of Prussian Blue (PB) produces Prussian White (ferrous ferrocyanide), which contains Fe(II) throughout the lattice, and Prussian Yellow (ferric ferricyanide), which contains Fe(III) in all iron positions.

The large spacing of the HCF lattice gives it a zeolite-type nature, with the interstitial spaces and many lattice sites filled with water molecules and electrolyte ions. In the presence of  $\text{K}^+$  ions, soluble compounds, known as Everitt's salt (potassium ferrous ferrocyanide,  $\text{K}_2\text{Fe}_2^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ ), soluble Prussian Blue (potassium ferrous ferricyanide,  $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ ), and Berlin Green ( $\text{K}_{1-x}\{\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]\}_x\{\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]\}_{1-x}$ ) may form. In each of these polymers, potassium ions are substituted for iron ions in the lattice structure. Hamnet et al.,<sup>16</sup> using ellipsometry and FT-IR, have shown that a conversion of insoluble Prussian Blue to soluble Prussian Blue is possible with potential cycling in  $\text{K}^+$  electrolyte.

In contrast to most studies of deliberate HCF formation and adsorption, this work has explored the experimental conditions under which the undesirable adsorption of only the soluble form of the hexacyanoferrate complexes occurs from the ferrocyanide/ferricyanide redox couple in KCl electrolyte. FT-IR spectroscopy was used to investigate the effects of the HCF complex on the redox characteristics of the redox couple as well as the reversibility of the adsorption process.

## EXPERIMENTAL SECTION

**Instrumentation and Electrodes.** All FT-IR spectra were obtained using an optical bench mounted externally to a Bio-Rad/Digilab FTS-60A spectrometer. The infrared beam passes through the contents of a thin-layer spectroelectrochemical cell twice as it is reflected off the surface of the electrode. A narrow-band mercury/cadmium/telluride (MCT) detector (Graseby Infrared, Fairfield, CT) is used to measure the optical signal. The spectroelectrochemical cell has been described previously.<sup>13,17</sup> The thin layer of electrolyte has been spectroscopically determined to be  $\sim 2 \mu\text{m}$  in thickness, which corresponds to a volume of  $\sim 0.1 \mu\text{L}$  between the electrode and the  $\text{CaF}_2$  infrared window. A CV-27 potentiostat (Bio-Analytical Systems, West Lafayette, IN) was used to control the electrode potential in all spectroscopic and electrochemical experiments.

The working electrode was an 8-mm platinum disk. A saturated calomel electrode (SCE) in a Luggin capillary was used as the reference electrode, and a platinum wire placed symmetrically around the working electrode served as the auxiliary electrode. All potentials are reported vs SCE. For measurements done in bulk solution, the platinum electrode was pulled  $\sim 1$  cm back from the  $\text{CaF}_2$  window into bulk solution.

**Experimental Conditions.** The electrochemical cell and the working electrode were prepared by soaking in concentrated  $\text{HNO}_3/\text{H}_2\text{SO}_4$  (1:1) followed by copious rinsing in Milli-Q water (Millipore Corp., Medford, MA). The working electrode was then polished using successively finer alumina powders (1.0, 0.3, 0.05  $\mu\text{m}$ ). After polishing, the electrode was sonicated in three changes of Milli-Q water for a total of 15 min.

Background spectra and voltammograms were obtained with analytical grade 1 M KCl. Experiments were performed with analytical grade 10 mM potassium ferrocyanide in 1 M KCl unless otherwise noted. All solutions were prepared using Milli-Q water.

**Spectral Acquisition and Calculation.** Spectroscopic data were calculated as absorbance (from the sample and a reference single-beam spectrum containing only electrolyte), a version of subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS),<sup>18</sup> or step-scan Fourier transform electrochemically modulated infrared spectroscopy (FT-EMIRS).<sup>19</sup> Conventional absorbance spectra were calculated using a single-beam spectrum obtained at a particular electrode potential referenced to a single beam spectrum obtained in 1 M KCl. The SNIFTIRS-type spectra were calculated as absorbance spectra in a similar fashion; however, each single-beam spectrum was measured in a solution containing both the redox couple and the electrolyte, but at different electrode potentials. Step-scan FT-EMIRS is a potential modulation technique which produces dynamic spectra that are the difference in the optical signal at the two different electrode potentials.<sup>13,17</sup> The single set of step-scan FT-EMIRS spectra shown in this paper are plotted as magnitude spectra, i.e., the vector addition of the two dynamic spectra obtained with this technique. All spectroscopic bands are positive in magnitude spectra, since they are the square root of the squared sum of the in-phase and quadrature spectra. The instrumentation and data acquisition methodology used for step-scan FT-EMIRS have been previously reported.<sup>13,17</sup>

## RESULTS AND DISCUSSION

**HCF Formation in Ferrocyanide.** Although some spectroscopic data on the ferrocyanide redox system indicate evidence of adsorbed species, initial work in our laboratory agreed with Christiansen,<sup>10</sup> in that only solution-phase ferrocyanide and ferricyanide were found. It was only after an experimental error in which the electrode potential was cycled over much larger potential limits ( $-0.33$  to  $+1.04$  V) than usual that the first appearance of an additional band in an EMIRS spectrum was noted. This result led us to investigate the effect of potential cycling in more detail. Three step-scan FT-EMIRS spectra taken after the electrode was cycled over the larger limits for  $\sim 1$  h are shown in Figure 2. For the first spectrum (Figure 2A) the total concentration of ferrocyanide and ferricyanide was 10 mM. At the end of this measurement the electrode was held at 0.40 V

(14) Jiang, M.; Zhao, Z. *J. Electroanal. Chem.* **1990**, *292*, 281.

(15) Bonnette, A. K., Jr.; Allen, J. F. *Inorg. Chem.* **1971**, *10*, 1613.

(16) Hamnet A.; Christensen, P. A.; Higgins, S. J. *Analyst* **1994**, *119*, 735.

(17) Budevská, B. O.; Griffiths, P. R. *Anal. Chem.* **1993**, *65*, 2963.

(18) Pons, S. *J. Electroanal. Chem.* **1983**, *150*, 495.

(19) Bewick A.; Kunitatsu, K.; Pons, S.; Russel, J. W. *J. Electroanal. Chem.* **1984**, *160*, 47.

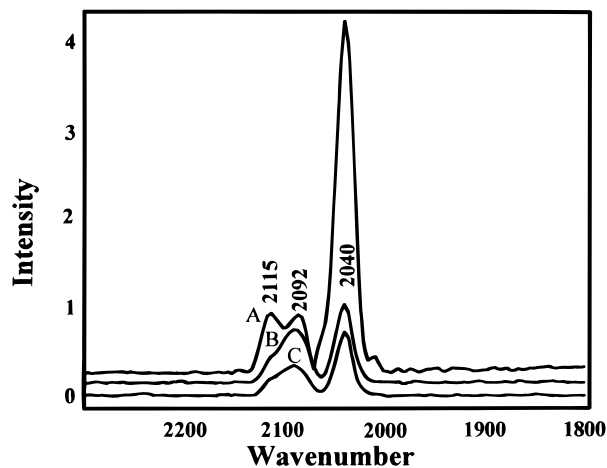


Figure 2. Step-scan FT-EMIRS spectra of ferrocyanide/ferricyanide after 1 h of potential cycling between  $-0.33$  and  $+1.04$  V at  $100$  mV/s. Concentration of ferrocyanide: (A)  $10$ , (B)  $1$ , and (C)  $0.1$  mM. Potential modulation frequency,  $1$  Hz; potential limits,  $0.02$  and  $0.42$  V.

and rinsed with  $1$  M KCl. The concentration of the redox couple was then reduced to  $1$  mM (Figure 2B) and finally to  $0.1$  mM (Figure 2C). As expected, the intensity of the solution-phase ferricyanide and ferrocyanide bands at  $2115$  and  $2040$   $\text{cm}^{-1}$ , respectively, decreases rather dramatically between  $10$  and  $1$  mM. A large broad band with an absorption maximum at  $2092$   $\text{cm}^{-1}$  is present in all three spectra. The intensity of this band is approximately constant during the first concentration reduction, suggesting that it is attributable to an adsorbed species which stays on the electrode during the rinsing process and which does not dissolve to an appreciable extent in the presence of  $1$  mM ferro-/ferricyanide. The fact that this band is observed in the EMIRS measurement indicates that some fraction of the species giving rise to this feature varies during the potential modulation. With the second 10-fold decrease in concentration (to  $0.1$  mM), the intensity of the  $2092\text{-cm}^{-1}$  band begins to decrease while the solution bands do not decrease in intensity as expected. The previous experiment showed that the rinsing process does not remove the adsorbed species and diffusion in and out of the thin-layer cell is very slow. Thus, the small change in concentration of the solution-phase species must be attributed to the dissolution and decomposition of the adsorbed species to reform solution ferricyanide and ferrocyanide during the measurement of the FT-EMIRS spectrum in  $0.1$  mM ferro-/ferricyanide. Repeated experiments indicated that the species causing the broad band at  $2092$   $\text{cm}^{-1}$  formed most quickly in ferrocyanide solutions that had been left to stand for  $24$  h or more. Repetitive cycling experiments were done to determine the smallest potential limits that would produce the adsorbed species. Based upon initial experiments, sequential combinations of potential limits were tested, holding the top potential at  $+0.80$  V and gradually decreasing the lower potential, and holding the lower potential constant at  $-0.33$  V and gradually increasing the positive potential. Intermediate combinations of potentials were also tested. The smallest potential limits that produced the adsorbed species were  $-0.33$  to  $+0.80$  V. There was no evidence of adsorbate formation unless the electrode was in the thin-layer geometry; i.e., pushed up against the infrared transparent window during potential cycling.

**Characterization of the Adsorbed Species.** Absorbance spectra were calculated from single-beam spectra collected at

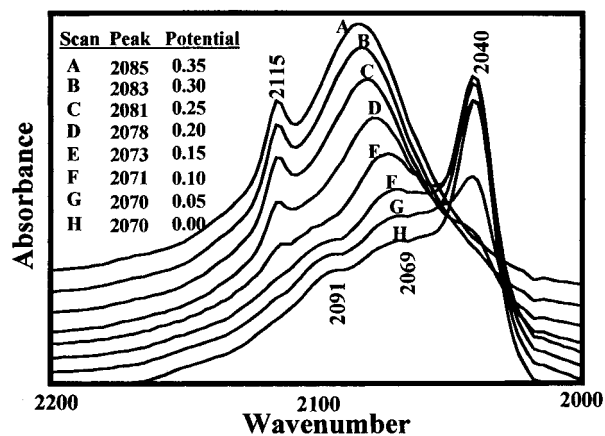


Figure 3. Absorbance spectra of ferro-/ferricyanide and adsorbed species as a function of electrode potential. Reference spectrum is that of  $1$  M KCl. Peak absorbances and electrode potentials are indicated.

electrode potentials between  $0.00$  and  $0.35$  V with the single-beam spectrum of  $1$  M KCl used as the reference. These spectra, shown in Figure 3, provide further evidence that the broad band should be attributed to an adsorbed species. Ferricyanide and ferrocyanide bands at  $2115$  and  $2040$   $\text{cm}^{-1}$ , respectively, increase or decrease in intensity with changing electrode potential but do not shift; i.e., they behave in a manner that is characteristic of solution species. In contrast, the intense broad band located between the bands due to solution-phase species shifts to higher wavenumber with increasingly positive electrode potentials. An effect similar to this, assigned to the electrochemical Stark effect,<sup>20</sup> has been reported with carbon monoxide adsorbed onto platinum electrodes. This shift in absorption maximum with changing electrode potential is often used to identify surface species. The change in intensity of the solution bands indicates that although the adsorbed species is present on the electrode, it does not completely impede electron transfer. At potentials below  $0.20$  V, two small bands are evident at  $2091$  and  $2069$   $\text{cm}^{-1}$ . As the potential increases and the intensity of the main band becomes stronger, these two bands become masked. Spectra collected at electrode potentials above  $0.35$  V showed little increase in the wavenumber of maximum absorption. A possible explanation for this is that all the iron centers from adsorbed species are converted to Fe(III) above  $0.35$  V. This explanation is validated by the voltammograms measured after different lengths of time potential cycling which show a diffusion-limited current above  $0.35$  V; see later (Figure 5).

The results of a SNIFTIRS-type experiment in which absorbance difference spectra were calculated from single-beam spectra collected at electrode potentials of  $0.42$  and  $0.02$  V (symmetric about  $E^0$ ) for cycling times from  $0$  to  $6.5$  h are shown in Figure 4. This procedure leads to spectra in which species present at the less positive potential ( $0.02$  V) result in upward-going bands and those present at the more positive potential ( $0.42$  V) result in downward-going bands. The bipolar band with a negative peak at  $2092$   $\text{cm}^{-1}$  and a positive peak at  $2070$   $\text{cm}^{-1}$  is a result of the shift in band position of the adsorbed species at the two different electrode potentials, as shown in Figure 2. The bipolar band increases in intensity with potential cycling time, indicating that it adsorbs onto itself after the electrode surface is covered. This

(20) Lambert, D. *Solid State Commun.* **1984**, *51*, 297.

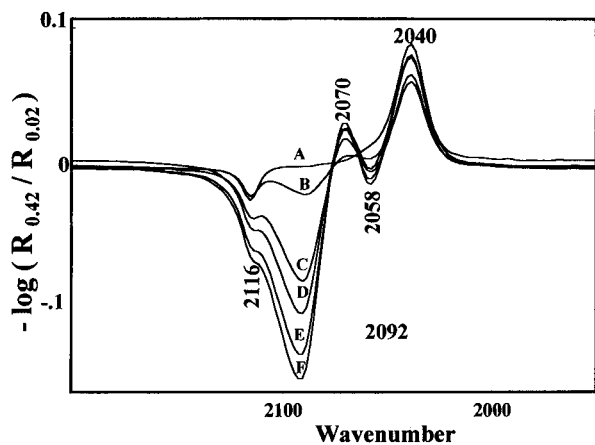


Figure 4. SNIFTIRS-type absorbance difference spectra measured as a function of time potential cycling between  $-0.33$  and  $+0.80$  V: (A) 0, (B) 150, (C) 180, (D) 210, (E) 270, and (F) 390 min. Single-beam spectra were measured at 0.02 and 0.42 V.

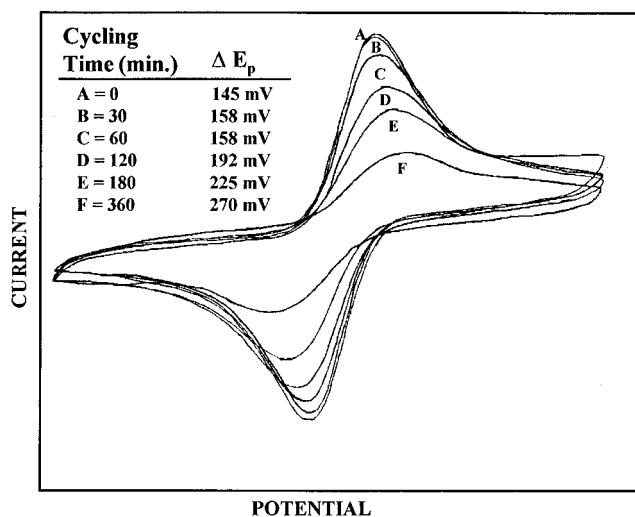


Figure 5. Cyclic voltammograms measured at 1-h intervals during potential cycling in 10 mM ferro-/ferricyanide solution: potential limits,  $-0.33$  to  $+0.80$  V; scan rate, 100 mV/s; time potential cycling, (A) 0, (B) 60, (D) 120, (E) 180, and (F) 360 min.

behavior is in contrast to molecules such as carbon monoxide, which saturate the surface with a simple chemisorbed molecular layer and then will adsorb no further. The solution-phase ferrocyanide band decreases in intensity as the bipolar band grows, indicating a decrease in the concentration of solution-phase ferrocyanide in the thin-layer cell. It is difficult to judge the change in intensity of the ferricyanide band, since its absorbance is increased by the wings of the bipolar band. The continual increase in adsorption (well beyond one monolayer) and the changes in band intensity suggest that this is a polymeric HCF complex formed from the solution-phase ferrocyanide and ferricyanide during potential cycling over large limits in the thin-layer cell.

Cyclic voltammograms measured in bulk solution at 1-h intervals during HCF adsorption are shown in Figure 5. As adsorption progresses, the separation of the anodic and cathodic peaks ( $\Delta E_p$ ) increases and the redox peaks broaden and decrease in intensity. However, there is no evidence of any voltammetric peaks associated with the adsorbed complexes Prussian White, Prussian Blue, or Prussian Yellow between  $-0.33$  and  $+0.80$  V. The voltammogram of Prussian Blue synthesized electrochemically according to eq 1 has large, pointed anodic and cathodic

Table 1. Measured Change in  $\Delta E_p$  and Calculated  $k^\circ$  as a Function of Time Spent Potential Cycling between  $-0.33$  and  $+0.80$  V vs SCE

time cycling (min)	$\Delta E_p$ (mV)	$k^\circ$
0	145	$2.0 \times 10^{-3}$
60	158	$1.8 \times 10^{-3}$
120	192	$1.2 \times 10^{-3}$
180	225	$5.5 \times 10^{-4}$
360	270	

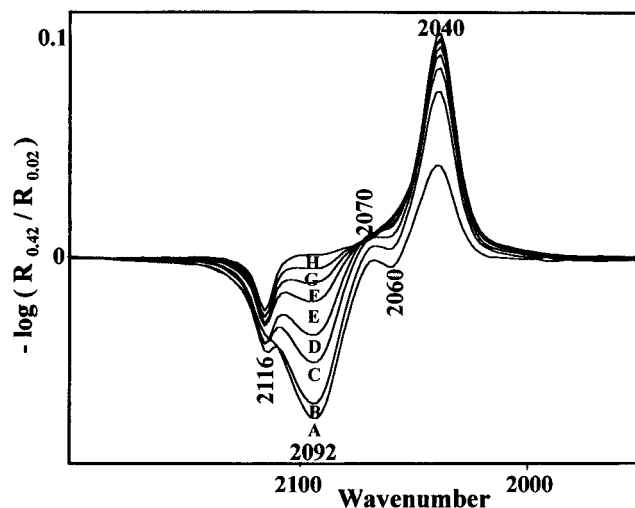


Figure 6. SNIFTIRS-type absorbance spectra collected at 1-h intervals after HCF adsorption with the electrode at open circuit potential in the thin-layer cell. Time at open circuit for A–H corresponds to 0–7 h. Single-beam spectra were measured at 0.02 and 0.42 V.

peaks with a measured  $E^\circ$  of  $\sim 0.2$  V vs Ag/AgCl, that should be discernible from that of solution-phase ferricyanide or ferrocyanide.<sup>16,21</sup> It is possible that these peaks are masked by the solution-phase ferro-/ferricyanide species; however as the film becomes thicker one would expect to see some evidence of their presence. Although the HCF complex does not completely impede electron transfer as its thickness increases, the electron-transfer rate for the ferrocyanide system decreases by a factor of  $\sim 4$  as estimated from the anodic and cathodic peak separation (see Table 1).

SNIFTIRS spectra showing the difference between data measured at 0.02 and 0.42 V indicate that, in contrast to the highly insoluble hexacyanoferrate complexes, this adsorbed species desorbs from the electrode readily at open circuit potential (see Figures 6 and 7). These spectra indicate that, in the thin-layer cell configuration, the HCF complex dissolves completely within 7 h. When the electrode is pulled away from the thin-layer geometry into bulk solution, the desorption occurs in a matter of minutes. Not only does the HCF desorb, but it appears to revert to solution-phase ferricyanide/ferrocyanide since there is no spectroscopic or voltammetric evidence of any other species in solution. Just as the formation of this complex decreased the intensity of the ferrocyanide peak, its dissolution increases the intensity of the ferrocyanide band, as shown in Figure 6. This evidence, along with the lack of any new bands assignable to solution-phase species, suggests a reversible process, in which the HCF can decompose and reform easily.

(21) Kulesza, P. J. *J. Electroanal. Chem.* **1990**, *289*, 103.

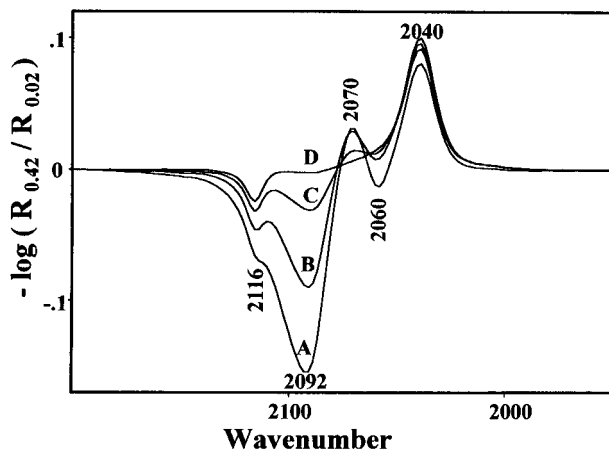


Figure 7. SNIFTIRS-type absorbance difference spectra collected at 2-min intervals after HCF adsorption with the electrode at open circuit potential in bulk solution. Time at open circuit for A–D corresponds to 0–8 min. Single-beam spectra were measured at 0.02 and 0.42 V.

These experiments provide a number of important clues as to both the identity and the prerequisites for the formation of the HCF complex in ferrocyanide solution with KCl electrolyte. First, the conclusion that both ferrocyanide and ferricyanide must be present in solution for HCF adsorption is suggested by the fact that the HCF complex forms faster with 1-day-old ferrocyanide (which is known to slowly oxidize to ferricyanide over time) than with a fresh ferrocyanide solution and that both the positive and negative extremes of the potential modulation are necessary for HCF formation to occur.

Second, the fact that the HCF complex only forms on the electrode when it is in the thin-layer geometry and that it desorbs and decomposes more quickly in bulk solution indicates that some equilibrium condition must exist in the thin-layer cell that is not present in bulk solution. As mentioned previously, Prussian Blue is generally synthesized by the reaction of ferric ion with ferrocyanide or ferrous ion with ferricyanide in an acidic medium. (pH 1) Thus, one possible explanation for Prussian Blue formation in neutral, aqueous solution and slower desorption/decomposition within the thin layer may be that a slightly acidic pH results within the thin-layer cell from the oxidation of water and concomitant production of  $\text{H}_3\text{O}^+$ . In fact, we have visibly seen Prussian Blue form in cracks on our Teflon electrode holder after soaking in an acid bath if extensive rinsing is not done to remove the acid completely before our electrochemical experiments in the ferri-/ferrocyanide redox couple are begun. An increased concentration of  $\text{H}_3\text{O}^+$  appears to drive the equilibrium of the reaction toward the formation of the soluble HCF complex. In bulk solution, the  $\text{H}_3\text{O}^+$  concentration is unchanged throughout the experiment, thus favoring dissolution of the complex.

A third criterion for the formation of a HCF complex from ferrocyanide and KCl electrolyte solution is that a source of the ferric or ferrous ion must be present. It has been suggested that solution-phase ferrocyanide or ferricyanide may decompose over time during potential cycling to produce these ions;<sup>7,22</sup> however, there is ample evidence that this decomposition does not occur to an appreciable extent. For example, in experiments using a 1:1 stoichiometric ratio of fresh ferricyanide to ferrocyanide, the

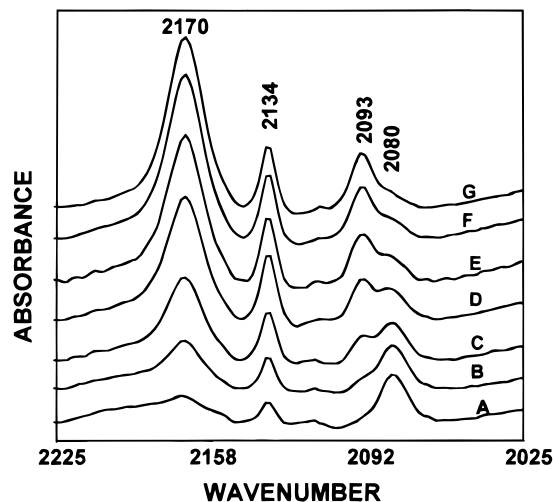


Figure 8. Absorbance spectra of 0.1 M NaCN with 1 M  $\text{K}_2\text{SO}_4$  electrolyte as background measured at 0.100-V potential intervals: (A) 0.35, (B) 0.45, (C) 0.55, (D) 0.65, (E) 0.75, (F) 0.85, and (G) 0.95 V.

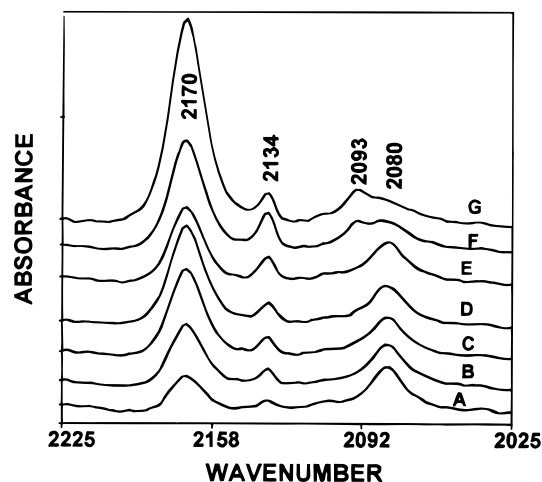


Figure 9. Absorbance spectra of 0.1 M NaCN with 1 M KCl electrolyte as background measured at 0.100-V potential intervals: (A) 0.35, (B) 0.45, (C) 0.55, (D) 0.65, (E) 0.75, (F) 0.85, and (G) 0.95 V.

HCF complex formed nearly as quickly as in old ferrocyanide solution. This suggests that the formation of ferricyanide, rather than a decomposition product, is important in HCF formation. In addition, the formation of totally or partially hydrated  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  ions would also produce free cyanide ions in solution. There is no spectroscopic evidence of solution-phase or adsorbed cyanide ions or any of the cyanoplatinate complexes which form from free cyanide solution on a platinum electrode. In solutions containing 0.1 M NaCN with both KCl and  $\text{K}_2\text{SO}_4$  electrolyte at potentials below +0.35 V (in sulfate) and below 0.85 V (in chloride), a solution-phase cyanide band can be observed at  $2080\text{ cm}^{-1}$ ; see Figures 8 and 9. Above these potentials, cyanide adsorbs onto the electrode surface as indicated by the band shift to  $2093\text{ cm}^{-1}$ . Absorption bands at  $2170$  and  $2134\text{ cm}^{-1}$  are probably assignable to cyanoplatinate complexes. The assignments were made by comparison to the results of Kunimatsu et al.<sup>23,24</sup> who studied the adsorption of free cyanide on silver and attributed the higher

(22) Pons, S.; Data, M.; McAleer, J. F.; Hinman, A. S. J. *Electroanal. Chem.* **1984**, *160*, 369.

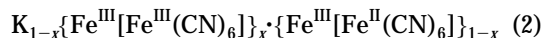
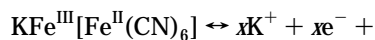
(23) Kunimatsu, K.; Seki, H.; Golden, W. *Chem. Phys. Lett.* **1984**, *108*, 195.

(24) Kunimatsu, K.; Seki, H.; Golden, W.; Gordon, J., II *Surf. Sci.* **1985**, *158*, 596.

wavenumber bands to solution and surface silver cyanide complexes. Platinum appears to form complexes similar to those of silver, beginning at potentials as low as  $-0.55$  V, but becoming very obvious at potentials above  $0.35$  V. While absorption bands due to low concentrations of solution-phase and adsorbed cyanide might easily be masked by the larger ferro-/ferricyanide and HCF bands, the presence of cyanoplatinate bands at  $2170$  and  $2134$   $\text{cm}^{-1}$  should be visible, particularly before any HCF adsorption.

**HCF Identification.** Identification of the HCF complex produced during potential cycling can be deduced from the following information. Insoluble Prussian Blue formed by chemical or electrochemical deposition processes is dark blue and both Prussian Blue and Prussian White adsorb irreversibly onto a platinum electrode.<sup>25</sup> In our experience, removal is difficult and can only be accomplished with concentrated acid or polishing of the electrode surface. We see no evidence of either of these characteristics, suggesting that these well-characterized insoluble complexes are not forming during our experiments. Since the potential cycling reported here is done in KCl electrolyte, one of the soluble HCF complexes, soluble Prussian Blue, Everitt's salt, or Berlin Green, seems to be a likely candidate. There is agreement between some of the characteristics of these compounds and the HCF complexes that we observe. For example, the HCF complex reported here cannot be visibly seen on the electrode surface; this is also true for Everitt's salt, which is colorless.<sup>26</sup> Berlin Green is reportedly yellow or greenish and hence may be difficult to see in the presence of ferricyanide solution species; however, we find no visible evidence of the adsorption process at any electrode potential. Our voltammetric data are unenlightening in terms of identifying the adsorbed species, since only redox peaks associated with the solution ferrocyanide and ferricyanide appear in the voltammograms and the redox peaks have a normal shape rather than the symmetric, pointed shape common to adsorbed species.

Our interpretation of these data is that a soluble HCF complex is forming which adsorbs strongly onto the electrode surface at positive potentials as either soluble Prussian Blue or Berlin Green, both mixed-valency soluble complexes. Using this assumption, the increased intensity and wavenumber shift of the large band at positive potentials shown in Figure 3 can be interpreted as being due to the formation/adsorption of potassium ferrous ferricyanide ( $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ ) followed by electrochemical conversion of most iron centers to Fe(III) at increasingly positive potentials to form a soluble complex containing both ferric ferricyanide and ferric ferrocyanide ( $\text{K}_{1-x}\{\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]\}_x \cdot \{\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]\}_{1-x}$ ) as shown in eq 2 below, where  $x$  is expected to be  $0.7-0.9$ . The relatively



easy desorption/dissociation of these complexes upon potential cycling explains the lack of evidence for their formation in the voltammograms, since they only adsorb strongly at positive potentials. As the reduction process occurs, these complexes desorb, decompose to solution ferricyanide, and are reduced to ferrocyanide (the presence of which can be implied from the cyclic voltammograms).

(25) Pharr, C. M., unpublished results.

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

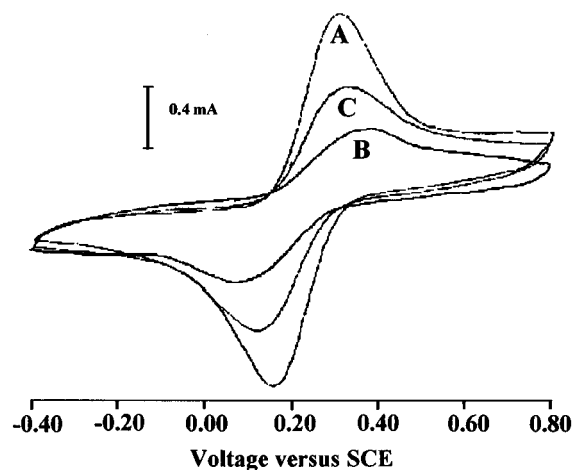


Figure 10. Cyclic voltammograms of ferri-/ferrocyanide after HCF desorption: (A) before potential cycling, (B) after 6 h of potential cycling, and (C) after standing at open circuit for 24 h.

For CO adsorbed on transition metal electrodes, the wavenumber shift observed on varying the electrode potential has been ascribed to a change in the force constant of the CO stretch due to either interactions with the polarizable electrons on the CO molecules (Stark effect)<sup>20</sup> or changes in electron donation into antibonding orbitals on the CO molecule (antibonding orbital theory).<sup>27</sup> However, the wavenumber shift associated with the adsorbed HCF complex cannot be interpreted by use of either of these hypotheses. The HCF complex reported here adsorbs onto the electrode surface as a polymeric compound rather than a monolayer, with iron atoms in both the +2 and +3 oxidation states. At increasingly positive potentials, more iron atoms are oxidized and the peak maximum for the  $\text{C}\equiv\text{N}$  stretch shifts to higher a wavenumber. At a sufficiently positive potential (above  $0.35$  V), most of the surface iron ions are in the +3 state and no further oxidation of iron in the HCF lattice occurs. The large full width at half-height of this peak is explained by the presence of CN ligands attached to both iron(II) and iron(III). Unfortunately, while a correlation between the spectroscopy and the thin-layer cyclic voltammetry would be extremely helpful in verifying this explanation, the large size of the working electrode causes the nonfaradaic current to swamp the voltammogram in the thin-layer configuration. All voltammetric data shown thus far are done by performing the cycling experiments in the thin layer and then pulling the electrode into bulk solution and quickly measuring the voltammogram. In this case, pulling the electrode into bulk solution produces a regular solution species voltammogram with very sluggish kinetics. (Figure 5F).

**Reversibility.** Although the spectroscopic evidence in Figures 6 and 7 indicates that the HCF complex completely dissolves from the electrode surface with time, the voltammograms shown in Figure 10 suggest that while the electrode kinetics improve after HCF removal (compare voltammograms B and C), they do not return to the original rate (A). In fact, a  $\sim 65\%$  recovery in electrode kinetics is the best obtained even if the electrode is left at open circuit for hours after the HCF has dissolved. The apparent reason for this behavior is that, despite the absence of the polymeric complex, ferrocyanide and ferricyanide themselves adsorb onto platinum electrodes as monomers and decrease the rate constant<sup>13</sup> in ferrocyanide solution that has been extensively

(27) Korzeniewski, C.; Pons, S. *J. Chem. Phys.* **1986**, *85*, 4153.

potential cycled. Based upon our discussion in the accompanying paper,<sup>13</sup> one would not expect to see evidence of these surface bands from adsorbed ferrocyanide or ferricyanide in a SNIFTIRS spectrum.

#### CONCLUSIONS

This work has shown that a soluble HCF complex forms with potential cycling over large potential limits within the thin-layer cell. We suggest that this colorless, soluble complex is a mixed-valency potassium HCF complex which gradually desorbs and decomposes at potentials less than 0.10 V. The experimental conditions required for formation of the HCF complex suggest that it is not responsible for the changing rate constants observed for this redox system under mild potential cycling experiments in bulk solution. Previous work by a number of groups indicates that ferrocyanide and ferricyanide themselves adsorb onto the electrode surface, and at least in KCl electrolyte, adsorption of one or both of these anions is the most likely cause of changes in

the electron-transfer rate constant. While our conclusions are only applicable to the ferrocyanide/ferricyanide redox system in KCl electrolyte, they suggest factors that may affect the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  redox system in other electrolytes.

#### ACKNOWLEDGMENT

Financial support for C.M.P. from Eastman Kodak in the form of a fellowship from the Analytical Division of the American Chemical Society is gratefully acknowledged. The authors are also grateful to the Digilab Division of Bio-Rad for donation of the FTS-60A step-scan spectrometer and for helpful discussions related to its operation.

Received for review November 5, 1996. Accepted August 23, 1997.<sup>⊗</sup>

AC961120L

---

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, October 1, 1997.