

# Electrochemical Behavior of Iron Hexacyanoferrate Monolayer Based on Metal Phosphonate Film

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The transition metal hexacyanoferrate belongs to a class of the insoluble mixed-valence compounds.<sup>1</sup> These compounds have the general formula of  $M^m_p[M^n(CN)_6]_q$  where  $M^m$  and  $M^n$  are transition metals with same or different oxidation states each other. According to their electronic conductivity, spectral characteristics and variable valence structures, the chemistry of metal hexacyanoferrates has been extensively studied.<sup>2</sup> Among transition metal hexacyanoferrates, the prototype is well known as Prussian blues (ferrous) ferro(ferri)cyanides). The basic structure of Prussian blue is a three-dimensional polymeric network consisting of alternating ferric and ferrous ions via bridging cyanide ligand in cubic lattice sites.<sup>3</sup> The remaining charge is balanced either by potassium ions as in Prussian blue ( $KFe[Fe(CN)_6]$ ) or by ferric ions as in Prussian blue ( $Fe_4[Fe(CN)_6]_3$ ). The only difference in these insoluble Prussian blues is dependent upon the degree of easiness in peptization with potassium ion. The chemical modification<sup>4</sup> of electrode by deposition of Prussian blues (PB) thin film has received much attention for the applications such as electrocatalysis,<sup>5</sup> electrochromic display devices<sup>6</sup> and electrochemical power sources.<sup>7</sup> To date, the electroactive PB films were prepared on conducting or semiconducting substrates by chemical and electrochemical methods.<sup>4-7</sup> However, these methods brought about the deposit of bulk microcrystalline PB on various electrodes of which film thickness was about a few micrometers.

Recently, Rao<sup>8</sup> and his coworkers first reported nickel and molybdenum hexacyanoferrate modification on electrode using self-assembled monolayer<sup>9</sup> of alkanolic acids. In this note, we report the preparation and voltammetric behaviors of PB (here,  $KFe[Fe(CN)_6]$ ) monolayer on gold by using self-assembly monolayer of alkylphosphonate. The reason of choosing phosphonate instead of carboxylate is that the ionic bonding between transition metal ion and phosphonate is basically much stronger than that of carboxylate due to larger basicity of phosphonate. Therefore, metal phosphonate provides more stable template for binding of PB monolayer than carboxylate network.

## Experimental

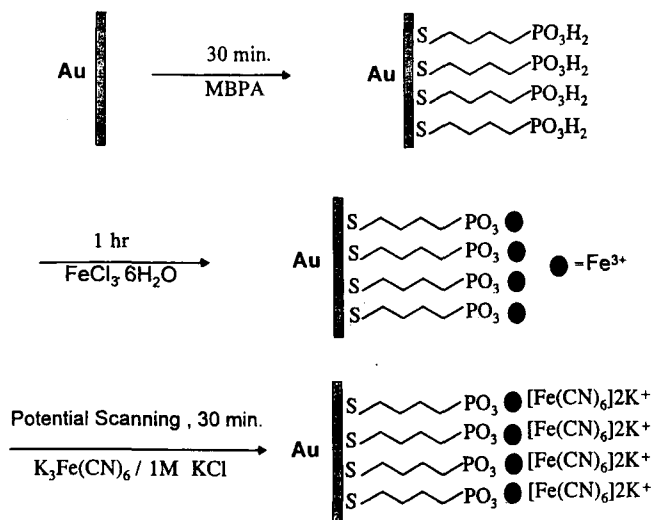
The electrochemical measurements were carried out in one-compartment cell with Au thin film electrode as working electrode, platinum counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. Voltammetric experiments were performed with the use of an EG&G/ PAR 273A Potentiostat coupled to a HP 7475A x-y plotter. The electrolyte solutions were prepared with deionized water purified to a resistivity of 18 M $\Omega$ /cm with UHQ II

(Elga) system and deaerated by purging with nitrogen.  $FeCl_3 \cdot 6H_2O$  (Aldrich),  $K_3Fe(CN)_6$  (Mallinckrodt), KCl (Merck) and all other chemicals were used as received. 4-Mercaptobutylphosphonic acid (MBPA) was synthesized as previously reported.<sup>10</sup>

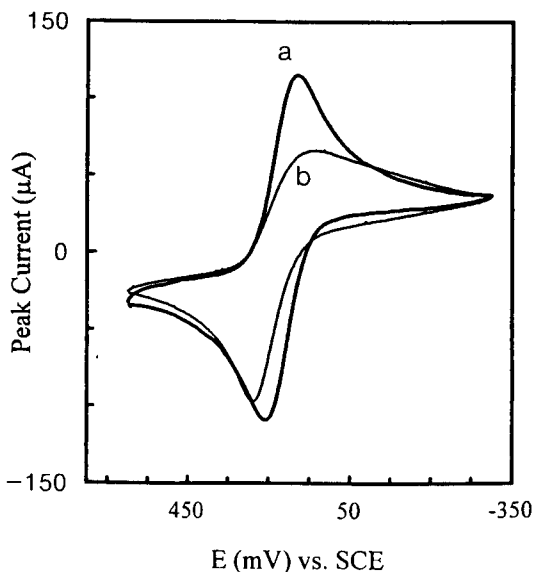
The Au thin film electrode (purchased from EMF Corp., Ithaca, N.Y.) was cleaned by sonication in chloroform followed by immersion for 10 s in a hot "piranha" solution (3:1 mixture of concentrated  $H_2SO_4$  and 30%  $H_2O_2$ ) prior to use. After rinsing with deionized water and drying with nitrogen gas blowing, gold electrode was immersed in 1 mM ethanol solution of MBPA for 30 min. The phosphonic acid-modified surface was washed thoroughly with ethanol and water, and then dipped in unbuffered 1 M KCl solution containing 10 mM  $FeCl_3$  for 1 h. Subsequently, the iron(III)-treated surface was thoroughly rinsed and potentially cycled between 0.0 V and 0.5 V in 1 M KCl containing 1 mM  $K_3Fe(CN)_6$  at 100 mV/sec for 30 min. The electrode was then rinsed and used for voltammetric studies.

## Results and Discussion

Scheme 1 shows the procedure used to prepare electroactive iron hexacyanoferrate ( $FeHCF$ ) monolayer on Au electrode surface. The treatment of Au surface with 4-mercaptobutyl phosphonic acid (MBPA) gave self-assembled monolayer of organic alkylphosphonate film on Au substrate. This MBPA monolayer has been employed as tem-



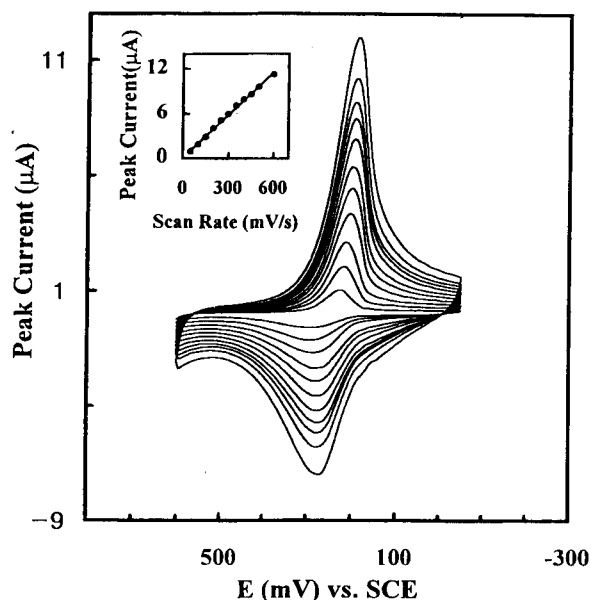
**Scheme 1.** Sequential procedure of preparation of iron hexacyanoferrate ( $FeHCF$ ) monolayer film on gold electrode modified with 4-mercaptobutylphosphonic acid (MBPA).



**Figure 1.** Cyclic voltammograms of bare gold (a) and MBPA modified gold (b) electrodes in 1 M KCl solution containing 1 mM  $\text{Fe}(\text{CN})_6$ . Scan Rate: 100 mV/sec.

plate for FeHCF deposition *via* phosphonate moiety of MBPA. In voltammetry, the Au electrode modified with MBPA yields background current which is practically the same as that obtained on bare Au in 1 M KCl (data not shown). Figure 1 shows voltammetric responses for bare Au and modified Au electrodes in 1 M KCl solution containing 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6$ . The faradaic peak current is decreased by one third of that on bare Au. And peak potential separation ( $\Delta E_p$ ) on Au/MBPA is increased to be 130 mV as compared to 65 mV on Au. These changes in voltammogram obviously indicate that MBPA monolayer makes electron transfer kinetics of ferricyanide slower. In the unbuffered KCl solution (*ca.* pH=6.8), iron(III) is easily coordinated to negatively charged phosphonate through electrostatic interaction. These ionic bondings seem to be fairly stable due to their large stability constants, which were reported from the measurement of the solid state coordination complexes of phosphonic acid with transition metal ions formed in aqueous solution.<sup>11</sup> After continuous potential cycling in ferricyanide solution, the Au modified with MBPA/FeHCF shows well-developed cyclic voltammograms due to realization of monolayer of iron hexacyanoferrate film (Figure 2). Though  $\Delta E_p$  of *ca.* 60 mV in this case is found to be greater than the peak separation for ideal surface wave, peak currents are shown to be proportional upto intermediate scan rate ( $0.6 \text{ V sec}^{-1}$ ). This fact is remarkable to be noted when compared to linearity of currents to square root of scan rates, which are typically observed on electrodes deposited with PB heavily.<sup>4-7</sup> However, it should be pointed out that the reason for the asymmetric peak shapes (shown in Figure 2) is mainly due to the hindered electron transfer of PB related to incorporation of potassium ion into the lattice structure of PB.

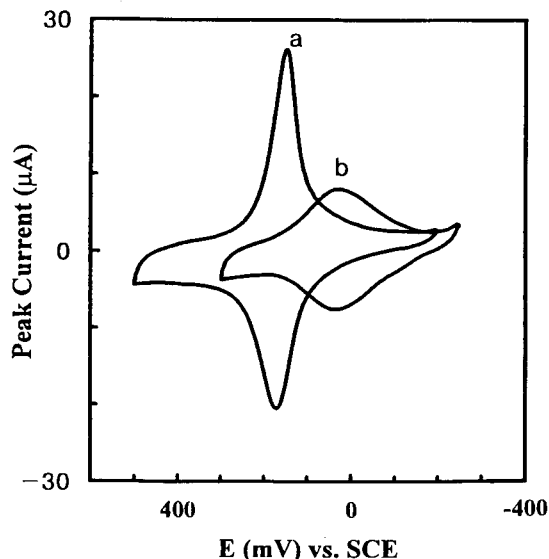
The crystal structure of PB is known to be simple face-centered cubic with a lattice constant of  $10.2 \text{ \AA}$ .<sup>12</sup> The packing density of PB monolayer can be calculated from lattice constant. The calculated value of monolayer coverage is



**Figure 2.** Cyclic voltammograms of FeHCF (Prussian blue,  $\text{KFe}[\text{Fe}(\text{CN})_6]$ ) monolayer film on gold in 1 M KCl solution. The inset is a plot of the cathodic peak currents against scan rate (mV/sec). The average surface coverage of PB monolayer is *ca.*  $4.3 \times 10^{-10} \text{ mole} \cdot \text{cm}^{-2}$ .

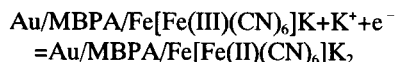
$6.4 \times 10^{-10} \text{ mole} \cdot \text{cm}^{-2}$ . The average surface coverage of FeHCF obtained from integration of voltammetric peak areas is *ca.*  $4.3 \times 10^{-10} \text{ mole} \cdot \text{cm}^{-2}$ . However, the difference in coverage can be rationalized due to vacancies of ferrocyanide ion in open structure of disordered PB layer on electrode surface. In fact, one fourth of lattice sites occupied with ferrocyanide is known to be vacant in normal PB structure.<sup>12</sup> With taking this into account, the deposition of PB using self-assembled monolayer technique seems to be a reasonable approach to obtain monolayer of FeHCF.

Prussian blues were reported<sup>4</sup> to show ionic permeability to penetrate into vacant sites of their spacious lattice structure. Figure 3 shows different voltammetric responses to alkali metal ions ( $\text{K}^+$  and  $\text{Na}^+$ ). The redox potential ( $E^0$ , taken as the average of the anodic and cathodic peak potentials) of PB monolayer is 0.148 V in 0.1 M KCl solution while 0.036 V in the equivalent concentration of NaCl. This observed potential difference indicates that PB monolayer can clearly recognize and discriminates  $\text{K}^+/\text{Na}^+$  ions like the bulk PB modified electrodes.<sup>4b,4c</sup> Rao<sup>8</sup> *et al.* recently reported alkali metal ion-selective behaviors by nickel hexacyanoferrate monolayer, which is similarly observed in our studies. The ionic discrimination and selectivity have been explained in terms of the hydrated ionic diameter and the channel size in metal hexacyanoferrate lattice for ionic transport. The voltammetric responses of PB monolayer to different concentration of potassium ion are shown in Figure 4. The peak potential shifts anodically as the molar concentration of potassium ion increases from 0.01 M to 3.0 M. Figure 5 shows that the redox potential shift is remarkably Nernstian with a slope of 58.8 mV per decade in the range of 0.01 M to 3.0 M of potassium ion concentration. This fact reveals that potassium ion plays an important role in the electrochemical reaction of PB monolayer. We propose

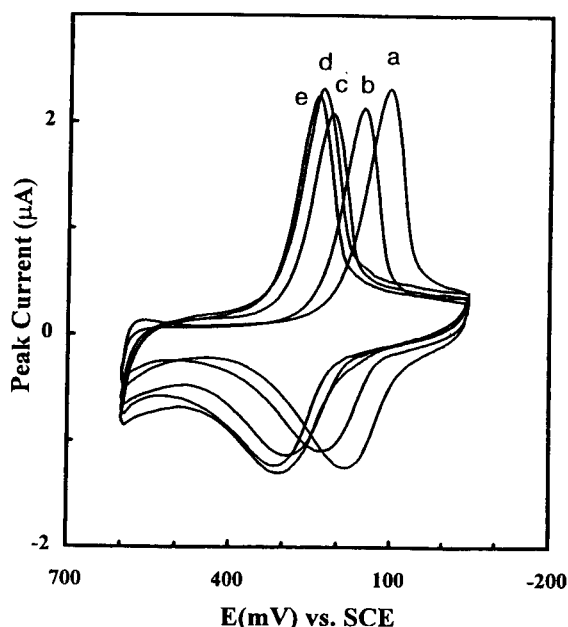


**Figure 3.** Cyclic voltammograms of FeHCF monolayer film on gold in different supporting electrolyte solution: (a) 0.1 M KCl; (b) 0.1 M NaCl. All scan rates: 100 mV/sec.

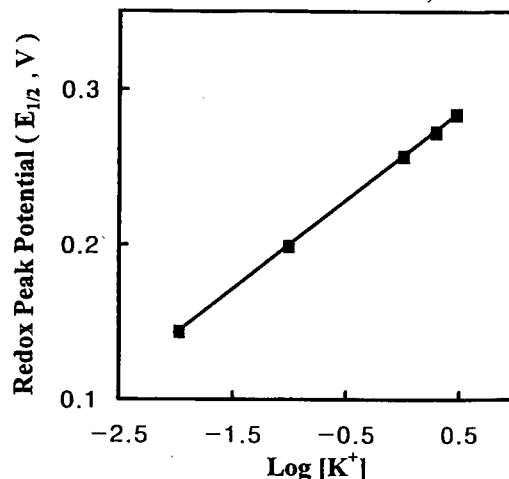
that PB monolayer on Au/MBPA template can be oxidized and reduced according to the following reaction:



$\text{KFe[Fe(CN)}_6\text{]}$ , one of the two famous PB forms, is formed by electrochemical cycling in the presence of excess potassium ion.<sup>4b</sup> There is still not complete agreement concerning the stoichiometric composition of Prussian blues because they are highly variable in their structure and stoichiometry. In fact, it is difficult for Prussian blues to as-



**Figure 4.** Cyclic voltammograms of FeHCF monolayer film on gold at different concentration of KCl solution: (a) 0.01 M; (b) 0.1 M; (c) 1 M; (d) 2 M; (e) 3 M. All scan rates: 100 mV/sec.



**Figure 5.** Plot of redox peak potential ( $E_{1/2}$ ) of FeHCF monolayer film vs. logarithm of molar concentration of potassium ion. Taken from data in Figure 4.

sign exact oxidation state of iron atoms consisting of PB because they are mixed-valence compounds in nature. When ferricyanide in  $\text{KFe[Fe(CN)}_6\text{]}$  formed on electrode is reduced to ferrocyanide, one  $\text{K}^+$  ion in solution phase is intercalated into  $\text{KFe[Fe(CN)}_6\text{]}$ . The completely reduced form of PB is  $\text{K}_2\text{Fe[Fe(CN)}_6\text{]}$  which is known as so-called Everitt's salt. In oxidation, potassium ion is deintercalated in order to maintain charge neutrality. It is interesting to note that an electron transfer reaction associated with metal ion transport results in ionic recognition by PB monolayer prepared on electrode. As shown in Figure 5, the PB modified Au electrode demonstrates ca. 150 mV of redox potential shift for two orders of electrolyte concentration range. The ability of tuning redox potential of PB by controlling electrolyte concentration can be exploited as a gate for electron transfer or activation/deactivation of electrochemical catalyst.

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## Dehydrogenation of Ketones by Palladium(II) trifluoroacetate-Phosphine and -Sulfide Systems

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Activation of carbon-hydrogen bonds is an important subject in organometallic chemistry. We have investigated the activation of aromatic carbon-hydrogen bond by Pd(OAc)<sub>2</sub>-phosphine system and have showed the system to be more effective than Pd(OAc)<sub>2</sub>-sulfide system.<sup>1</sup> Herein, we wish to report the activation of aliphatic carbon-hydrogen bond of cyclic ketones (cyclopentanone and cyclohexanone) using Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>-phosphine and -sulfide systems. Although many papers on the activation of aliphatic C-H bond have been published previously<sup>2-5</sup> and dehydrogenation reactions of cyclic ketones were studied by Fuchita *et al.* using Pd(OAc)<sub>2</sub>-SBU<sub>2</sub> system,<sup>6</sup> trifluoroacetate as an anion is an interesting choice for the following reasons: 1) the CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> ion is relatively weaker than CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> ion in basicity and M-O<sub>2</sub>CCF<sub>3</sub> bond is quite labile,<sup>2,7</sup> which can be dissociated more easily to give a vacant site of the metal complexes, 2) however, trifluoroacetate ligand might reduce the catalytic activity due to the poor basicity as well, and 3) trifluoroacetate does not contain C-H bond itself. Also, phosphine has been selected to compare the catalytic activity with the sulfide system. The reaction of cyclic ketone has been carried out for 5 hours in the presence of Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> with phosphine or sulfide (PR<sub>3</sub>=P(*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>3</sub>, P(*p*-C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub>, PPh<sub>3</sub>, P(OBu<sup>*n*</sup>)<sub>3</sub> and SR<sub>2</sub>=S(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, S{CH(CH<sub>3</sub>)<sub>2</sub>}<sub>2</sub>, S{CH(CH<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)}<sub>2</sub>, S(CH<sub>2</sub>Ph)<sub>2</sub>, S{C(CH<sub>3</sub>)<sub>3</sub>}<sub>2</sub>) at 75 °C in this work. The mechanism of dehydrogenation of cyclic ketones is considered to be the formation of α-palladated cyclic ketone followed by the formation of dehydrogenation

product from β-hydride elimination.<sup>6</sup>

The yield of 2-cyclohexen-1-one produced from cyclohexanone is highest (589%) when the molar ratio of Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> to P(*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>3</sub> is 1:2, while the highest yield was obtained for the molar ratio of 1:2/3 in Pd(OAc)<sub>2</sub>-SBU<sub>2</sub> system. The yields based on the amount of Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> used are the average value of three or four trials and have been measured on GC with hexadecane as an internal standard. Lower yields were obtained for the ratio of 1:2/3 (417%), 1:1 (513%) and others. Therefore, the molar ratio has been kept 1:2 for all of the reactions in this work to maintain the identical reaction condition. Although it is not clear for now, the ratio of 1:2 may suggest the structure of the intermediate involves two phosphine ligands coordinated to a palladium metal. Table 1 shows the yields of cycloalkenones catalyzed by Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>-phosphine and -sulfide systems. In dehydrogenation reaction of cyclohexanone, the highest yield (589%) of 2-cyclohexen-1-one has been afforded by P(*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>3</sub>, which includes the most basic substituent among the series of phosphines. It is interesting to point out P(*p*-C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub> gives more yield (363%) than PPh<sub>3</sub> (307%). The *para*-fluorine of the phenyl group seems to be rather electron donating than electron withdrawing due to the resonance effect. Yield is 275% in the absence of phosphine, which means Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> itself can activate the aliphatic C-H bond of ketone very well. For reference, the same reaction using Pd(OAc)<sub>2</sub> was carried out under the identical condition, and the yield is extremely low (28%), therefore, trifluoroacetate anion reinforces catalytic activity more than acetate does. On the other hand, P(OBu<sup>*n*</sup>)<sub>3</sub> containing an electronegative and bulky substituent gives much lower yield (39%) than Pd(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> itself. Therefore, more basic and less hindered phosphines<sup>8</sup> afford more products.

In case of sulfide series, S(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> affords the highest yield (422%) and the second yield (320%) is obtained for S{CH(CH<sub>3</sub>)<sub>2</sub>}<sub>2</sub> and SPh<sub>2</sub> gives 223% of the yield. It seems the sulfide with more basic substituent gives more yield than phosphine series. However, steric factor must be

