

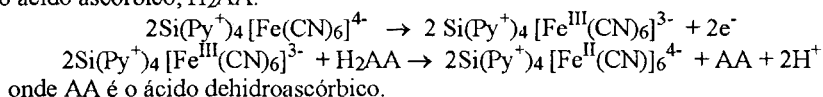
Cyclic Voltammetry Study of Hexacyanoferrate Complex Immobilized on Silica Gel Surface Chemically Modified With Pyridinium Ion

Lilian L. Lorencetti, Yoshitaka Gushikem*

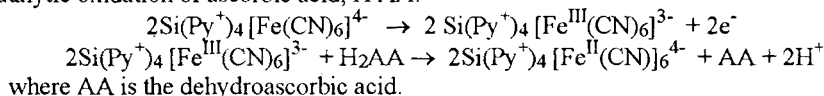
*Instituto de Química, Unicamp, CP 6154,
13081-970 Campinas, SP, Brasil*

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Silica gel quimicamente modificada com o íon piridínio foi utilizada para imobilizar o íon complexo hexacianoferrato através de uma reação de troca iônica. A espécie eletroativa imobilizada apresentou um potencial formal de superfície $E_o^s = 127\text{mV vs ECS}$ em NaCl usado como eletrólito suporte. O eletrodo de pasta de carbono confeccionado com este material foi muito estável e a quantidade de espécie eletroativa lixiviada da superfície após vários ciclos redox foi desprezível. A espécie eletroativa mediou a oxidação eletrocatalítica do ácido ascórbico, H₂AA:



The chemically modified silica gel with propylpyridinium ion was used to immobilize the hexacyanoferrate ion complex by means of ion exchange reaction. The immobilized electroactive species showed a formal surface potential $E_o^s = 172\text{ mV vs SCE}$ in NaCl used as the supporting electrolyte. A carbon paste electrode made with this material was very stable and the amount of the electroactive species leached from the surface after various redox cycles was very small. The immobilized electroactive species mediated an electrocatalytic oxidation of ascorbic acid, H AA:



Key words: silica gel; pyridinium ion; hexacyanoferrate ion.

Introduction

Electrodes coated with films of polymers or metal oxides have been used to immobilize anionic electroactive metal complexes by means of an ion exchange process¹⁻⁵. These systems have been investigated to determine the charge transport mechanism in the coating and for the purpose of catalysing or mediating redox reactions between the electrode and a substrate in the electrolyte⁶. When a complex like $[\text{Fe}(\text{CN})_6]^{3-/4-}$ is used, it remains in the coating films bound by electrostatic interaction⁷⁻¹⁰. In most of this system, a major limitation arises from the fact that *i*) the amount of the electroactive metal complex in the coating is pH dependent and *ii*) leaching of the electroactive species from the film surface may occur. In order to minimize the loss of the electroactive species due to the change of pH, pyridine in the 4-vinylpyridine film used as coating has been transformed to pyridinium ion¹¹. In this work, silica gel having high surface

area and chemically modified with pyridinium ion was used to incorporate and retain strongly the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ electroactive species. To diminish the internal electrical resistance of the silica matrix, the unreacted $\equiv \text{SiOH}$ groups were coated with Sn(IV) oxide following the process described in early work¹². The main advantage in using such material to attach the electroactive species has been the high chemical stability and the high exchange capacity shown by n-propylpyridinium chloride covalently bonded onto the silica gel surface¹³.

Experimental

The preparation of the propylpyridinium chloride immobilized on silica gel surface, $\equiv \text{Si}(\text{CH}_2)_3\text{-N}^+\text{C}_5\text{H}_5\text{Cl}^-$ was elsewhere described^{13,14}. About 20 g of this material, hereafter designated as SiPy^+Cl^- , was immersed in 100 ml of dry CCl_4 and then 15 ml of SnBr_4 was added. The mixture was care-

fully stirred at 353 K for 2 h under nitrogen atmosphere. The resulting product was filtered in a Schlenk apparatus under nitrogen atmosphere, washed with CCl_4 and finally with ethanol. The product was submitted to a careful hydrolysis with HCl solution (0.1 M) and dried for 8 h at about 353 K under vacuum.

The quantity of exchangeable chloride was determined by treating the material with 0.1 M HNO_3 solution and then the released Cl^- titrated with standard AgNO_3 solution. The quantity of the coating tin(IV) oxide was determined by X-ray fluorescence analysis. The results were: exchangeable chloride = $0.36 \times 10^{-3} \text{ mol.g}^{-1}$; coating tin(IV) = $0.07 \times 10^{-3} \text{ mol.g}^{-1}$.

The specific surface area determined by the B.E.T. multipoint method was $317 \text{ m}^2.\text{g}^{-1}$. The equipment used was the Micromeritics Flow Sorb 2300.

Ion Exchange Isotherms. The ion exchange isotherms were obtained by shaking 0.2 g of SiPy^+Cl^- with solutions of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ between 0.8×10^{-3} and $0.7 \times 10^{-5} \text{ M}$ for 2 h at 298 K. The quantity of iron in the supernatant solution was determined by atomic absorption spectrometry.

In an other experiment, 0.2 g of SiPy^+Cl^- was shaken in 50 ml of $1 \times 10^{-3} \text{ M}$ solutions of ferro- or ferricyanide in KCl solutions of variable concentration (between 0.1 and 1.0 M). The quantity of exchanged ferro- or ferricyanide ions, N_f , was calculated by applying the equation:

$$N_f = \frac{(N_a - N_s)}{m}$$

where N_a is the initial mole number and N_s is the mole number of the ferro- or ferricyanide ions in equilibrium with the solid phase and m is the mass of the solid.

The distribution coefficient, D , was calculated by applying the equation:

$$D = \frac{N_f}{C}$$

where C is the equilibrium concentration of ferro- or ferricyanide in the solution phase in equilibrium with the solid phase.

Infrared Spectra. The FT-IR spectra of the self supported disk of the material was obtained by the transmission technique according to the elsewhere described method¹⁵. The equipment used was a Perkin Elmer FT-IR 1600 spectrophotometer.

Cyclic Voltammetry Study. The cyclic voltammetry (CV) study of the material was carried out in a cell under highly pure nitrogen atmosphere. A carbon paste electrode made by mixing 40 mg of pure graphite, 30 mg of the material and few drops of a mineral oil was used as the working electrode. A platinum wire was used as the auxiliary electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The equipment used was an MRA potentiostat connected to an ECB X-Y recorder.

In order to study the electron mediator property of the material, in an electrochemical cell, 20 ml of 0.7 M of KCl solution was initially purged with pure nitrogen. The electrodes were settled as described above and then, 0.1 ml of ascorbic acid, H_2AA , 0.05 M was successively added. For each addition, the potential was swept between -0.2 and 0.5 V.

Results and Discussion

Exchange Isotherms. The amount of the exchanged Cl^- by the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ ions on SiPy^+Cl^- was determined using the isotherms shown in Figure 1. At saturation condition, the value of $0.090 \times 10^{-3} \text{ mol.g}^{-1}$ for ferrocyanide complex and $0.15 \times 10^{-3} \text{ mol.g}^{-1}$ for ferricyanide complex was found for N_f . Considering that the exchange capacity of SiPy^+Cl^- is $0.36 \times 10^{-3} \text{ mol.g}^{-1}$, we estimated the mol ratios $\{\text{SiPy}^+\text{Cl}^-\} : \{[\text{Fe}(\text{CN})_6]^{4-}\} = 4:1$ and $\{\text{SiPy}^+\text{Cl}^-\} : \{[\text{Fe}(\text{CN})_6]^{3-}\} = 2.6:1$.

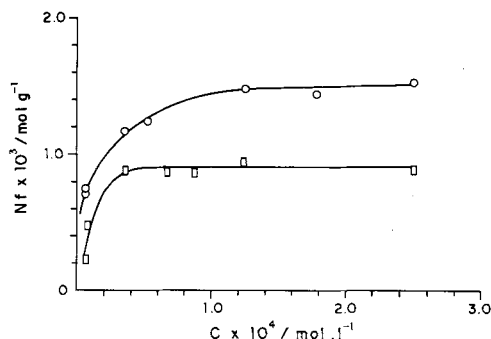


Figure 1. Exchange isotherms of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ on SiPy^+Cl^- in aqueous solution at 298 K. (o) $[\text{Fe}(\text{CN})_6]^{3-}$, (□) $[\text{Fe}(\text{CN})_6]^{4-}$.

The distribution coefficients for ferro- and ferricyanide in the solution containing KCl , in which the concentrations were changed between 0.1 and 1.0 M, were determined. The results are shown in Figure 2. Curve A for ferrocyanide and curve B for ferricyanide show that the affinity of the SiPy^+Cl^- for both ions is very high and leaching of the anionic complex from the surface by the electrolyte in concentration as high as 1.0 M was not significant.

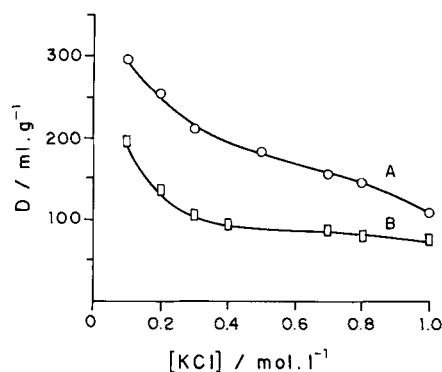


Figure 2. Distribution coefficients of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as function of KCl concentration: (curve A) $[\text{Fe}(\text{CN})_6]^{3-}$, (curve B) $[\text{Fe}(\text{CN})_6]^{4-}$.

Cyclic voltammetry study. Silica gel matrix has a large internal resistance and in order to increase the conductivity, the remaining free $\approx\text{SiOH}$ groups in SiPy^+Cl^- were reacted with SnBr_4 and the surface was covered with tin(IV) oxide. The coating of the surface can be represented by the following reaction equations:

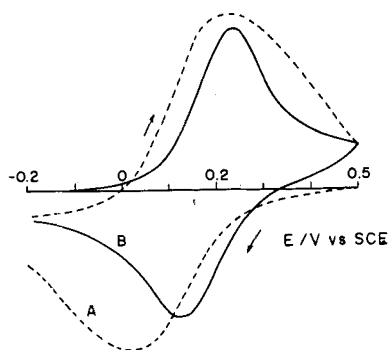
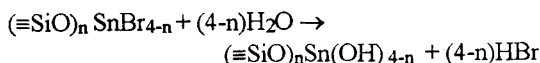
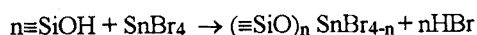


Figure 3. Cyclic voltammograms of: (A) uncoated $\text{Si(Py}^+)_{3/4} [\text{Fe}(\text{CN})_6]^{3-/4-}$, (B) SnO_2 coated $\text{Si(Py}^+)_{3/4} [\text{Fe}(\text{CN})_6]^{3-/4-}$.



The effect of the internal resistance decrease on the shape of current vs potential waves can be observed comparing Figure 3A (dotted line) and Figure 3B (full line), respectively, for uncoated and tin(IV) oxide coated $\text{Si(Py}^+)\text{Cl}^-$. For tin(IV) oxide coated $\text{Si(Py}^+)_{3/4} [\text{Fe}(\text{CN})_6]^{3-/4-}$ in Figure 3B the value of ΔE ($\Delta E = E_{pa} - E_{pc}$; E_{pa} and E_{pc} are, respectively, the anodic and cathodic peak potentials) is considerably smaller than that observed for uncoated $\text{Si(Py}^+)_{3/4} [\text{Fe}(\text{CN})_6]^{3-/4-}$ i.e., respectively, 80 and 200 mV. In this work, unless otherwise stated, the chemically modified silica will always refer to the tin(IV) oxide coated $\text{Si(Py}^+)_{3/4} [\text{Fe}(\text{CN})_6]^{3-/4-}$.

The electroactive species under potential sweeping between -0.30 and 0.50 V, in 0.7 M KCl supporting electrolyte and scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$, was shown to be very stable. The I_{pa} and I_{pc} values were measured as a function of time (Fig. 4). After 14 redox cycles, the decrease in the peak currents, I_{pa} and I_{pc} , was attributed as due to the leaching of the electroactive species from the surface which may occur by an ion exchange process⁵.

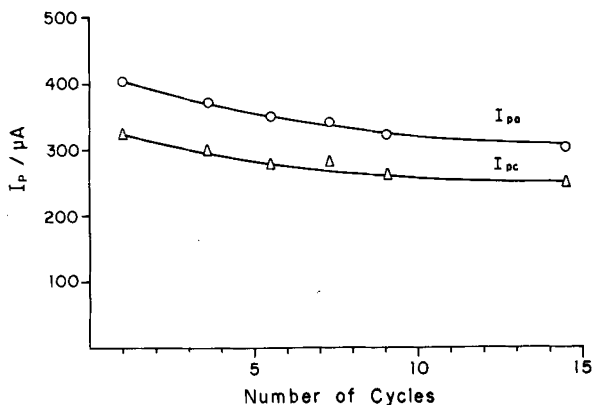


Figure 4. Current peaks vs. number of redox cycles for $\text{Si(Py}^+)_{3/4} [\text{Fe}(\text{CN})_6]^{3-/4-}$.

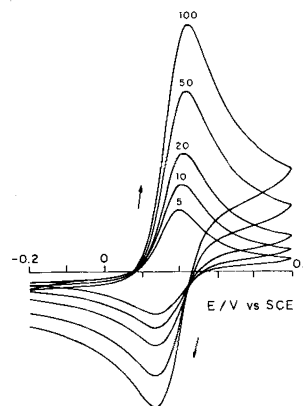
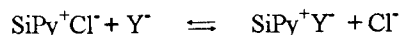


Figure 5. Cyclic voltammograms for SiPy^+/HCF at various sweeping velocities: 5, 10, 20, 50 and 100 refer to scan velocities (in $\text{mV}\cdot\text{s}^{-1}$).

The sweep velocity in 1.0 M NaCl supporting electrolyte solution was varied between 5 and $100 \text{ mV}\cdot\text{s}^{-1}$, resulting in a set of voltammograms shown in Figure 5. The main parameters are listed in Table 1. The surface potential, E_s^0 , is $172 \pm 5 \text{ mV}$. This value is the same as that found for HCF adsorbed⁴ on $\text{TiO}_2/\text{SiO}_2$, i.e. 175 mV, and slightly lower as that found for the formal potential of the couple $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in $\text{SnO}_2/\text{SiO}_2$ and in aqueous solution i.e. 220 mV^{16,17}. The separation of the peak potentials, ΔE_p , showed only a small increase as the sweep potential was increased from 5 to $100 \text{ mV}\cdot\text{s}^{-1}$ indicating that the kinetic of the electron transfer process is considerably fast in this case.

A linear relationship was obtained (Fig. 6) when the concentration of NaCl supporting electrolyte was varied between 0.2 and 1.0 M and the values of E_s^0 plotted against $\log([\text{NaCl}]/\text{mol}\cdot\text{l}^{-1})$. The slope of the line corresponded to 47 mV, therefore lower than 59 mV per decade of the NaCl concentration change, expected from a Nernstian behavior.

Influence of the Anion on the Surface Potential. Considering the exchange reaction:



The selective constant, K , can be defined by the equation:

$$K = \frac{a_Y a_{ce}}{a_{ce} a_Y}$$

where \bar{a}_Y and \bar{a}_{Cl} are the activities of the Y^- and Cl^- in the

Table 1. Cyclic voltammetry parameters obtained for $\text{Si(Py}^+)_{3/4} [\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.7 M NaCl solution at room temperature.

V $\text{mV}\cdot\text{s}^{-1}$	I_{pa} mA	I_{pc} mA	E_{pa} mV	E_{pc} mV	E_s^0 mV
5	34	22	200	135	167
10	48	31	208	135	171
20	67	42	210	135	172
50	103	67	215	130	172
100	139	65	215	130	177

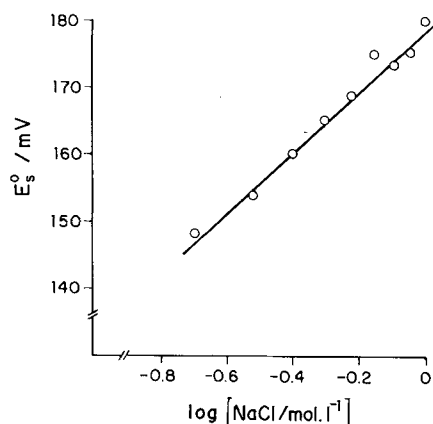


Figure 6. Surface potential plotted against the NaCl concentrations (mol/l) for $\text{Si(Py}^+)_{3/4}[\text{Fe}(\text{CN})_6]^{3-/4-}$.

solid phase and a_{Cl} and a_{Y} are the activities of Cl^- and Y^- in the solution phase.

The selectivity constant for a serie of anions have been determined for the immobilized cationic species^{13,17} SiPy^+ . These constants were small for many of anions studied but K was particularly great for perchlorate anion. Therefore, the influence of this anion was studied in the redox process as it was used as the supporting electrolyte. The voltammograms in NaCl 1.0 M and in NaClO_4 1.0 M solutions are compared in Figure 7. It can be observed that the position of the anodic peak is nearly the same for both electrolytes, nearly at 230 mV, while the cathodic peaks are observed at 123 and 190 mV for NaCl and NaClO_4 supporting electrolytes, respectively. Such influence can be explained by considering the reaction:

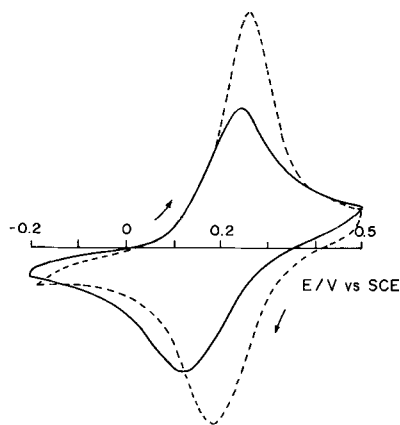
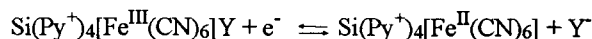


Figure 7. Cyclic voltammograms for $\text{Si(Py}^+)_{3/4}[\text{Fe}(\text{CN})_6]^{3-/4-}$ obtained in: 1.0 M NaCl (full line) and 1.0 M NaClO_4 (dotted line). Scan rates for both electrolytes: $10 \text{ mV}\cdot\text{s}^{-1}$.



If the affinity of Y^- by the solid phase is high (larger selectivity constant), it is expected that for this anion the reduction will occur at a more positive potential in comparison with that anion having lower affinity for the solid phase. In 1.0 M NaClO_4 solution, the surface potential is 222 mV and in 1.0 M 2NaCl solution, it is 170 mV.

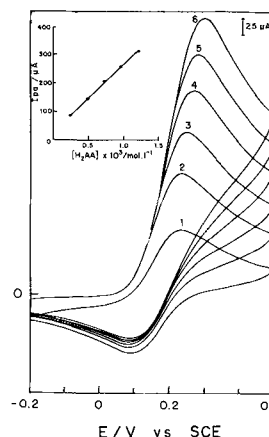
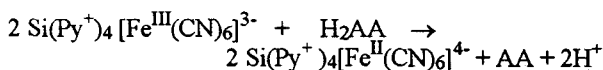
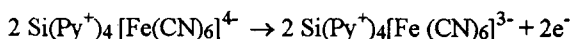


Figure 8. Cyclic voltammograms for $\text{Si(Py}^+)_{3/4}[\text{Fe}(\text{CN})_6]^{3-/4-}$ obtained after successive additions of ascorbic acid. Voltammograms: 1) absence of H_2AA ; 2) $[\text{H}_2\text{AA}] = 0.25 \times 10^{-3} \text{ M}$; 3) $[\text{H}_2\text{AA}] = 0.50 \times 10^{-3} \text{ M}$; 4) $[\text{H}_2\text{AA}] = 0.98 \times 10^{-3} \text{ M}$ and 5) $[\text{H}_2\text{AA}] = 1.20 \times 10^{-3} \text{ M}$. Concentration of the NaCl supporting electrolyte = 0.7 M; scan rate = $10 \text{ mV}\cdot\text{s}^{-1}$. Inset Figure: I_{pa} vs. concentration of the ascorbic acid.

Electron Mediator Property. Ferrocyanide ion, electrostatically bonded on a thin film of organic polymer coated on the electrode, has been used in electrocatalytic oxidation of ascorbic acid^{13,18-20}. One reaction is the self catalytic electron exchange process by which many of the immobilized $[\text{Fe}(\text{CN})_6]^{4-}$ are oxidized by the electrode surface and the second is the electrocatalytic oxidation of ascorbic acid in the solution phase by $[\text{Fe}(\text{CN})_6]^{3-}$ electrogenerated in the film. This study was extended to the $\text{Si(Py}^+)_{3/4}[\text{Fe}(\text{CN})_6]^{3-/4-}$ electrode in order to evaluate its ability to mediate the electrocatalytic oxidation of ascorbic acid. Figure 8 shows the CV wave for $\text{Si(Py}^+)_{4}[\text{Fe}(\text{CN})_6]^{4-}$ in the absence of ascorbic acid and the CV waves obtained by successive addition of known amount of ascorbic acid, H_2AA . The magnitude of the I_{pa} subtracted for the anodic peak current in absence of H_2AA , is plotted against the concentration of ascorbic acid (Inset of Fig. 8). The correlation coefficient of the straight line was 0.99. The reactions that occur at the interface of the electrode can be represented by the following equations:



where AA is the dehydroascorbic acid.

Conclusions

The high affinity of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ for SiPy^+Cl^- , allowed to fabricate an electrode in which the electroactive species was strongly bonded to the counterion covalently bonded to the surface. The monolayer of the attached electroactive species (surface density of $0.17 \text{ molecule.nm}^{-2}$) was chemically very stable and electrocatalyzed the oxidation of ascorbic acid. The advantage in using this electrode was the negligible loss of activity after various redox cycles. This result indicates that $\text{Si}(\text{Py}^+)_{3/4}[\text{Fe}(\text{CN})_6]^{3-/4-}$ potentially can be used to fabricate a chemical sensor for ascorbic acid.

Acknowledgments

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