Chim. Acta **1992**, *260*, 1.
15. Kirchnerova, J.; Purdy, W. C. *Anal. Chim Acta* **1981**, *123*, 83.
16. Grigorova, B.; Wright, S. A. *J. Chromatogr.* **1986**, *368*, 444.
17. Fleet, B.; Little, C. J. *J. Chromatogr. Sci.* **1974**, *12*, 747.
18. Tenygl, J. in *Electrochemical Detectors*; Ryan, T. H. Ed.; p 89, Plenum Press: New York, 1984.
19. Johnson, D. C.; LaCourse, W. R. *Anal. Chem.* **1990**, *62*, 589A.
20. LaCourse, W. R.; Johnson, D. C. *Anal. Chem.* **1993**, *65*, 50.
21. Bard, A. J.; Faulkner, L. R. in *Electrochemical Methods*; p 143, John Wiley & Sons: New York, 1980.

Electrochemical Behavior of the Reduction of Thin Films of $Ag_3Fe(CN)_6$

Seongbae Moon* and Jung Dae Moon

Department of Chemistry Education, Pusan National University, Pusan 609-735, Korea
Received May 28, 1994

A thin film of silver ferricyanide ($Ag_3Fe(CN)_6$) on a platinum or gold substrates can be reduced electrochemically to the salt of silver ferrocyanide in potassium nitrate solution. The color of these films are orange and these films are shown to be electrochromic. The voltammogram is shown the asymmetry of the oxidation compared to the reduction wave under various supporting electrolytes. The standard heterogeneous electron-transfer rate for these films and bare Pt electrode were 0.49×10^{-2} and 1.30×10^{-2} cm/s, respectively, obtained using a rotating disc electrode. Rough D_o values, evaluated from the Levich equation, for $Fe(CN)_6^{3-/4-}$ at both SF thin film and a bare Pt disc electrode were shown as 1.21×10^{-6} and 0.94×10^{-6} cm^2/s, respectively. The conductivities, as determined from the slops of the *i*-V curves for a *ca.* 1 mm sample for dried SF potassium rich and deficient bulk samples pressed between graphite electrodes, were 9.34×10^{-9} and 5.80×10^{-9} $(\Omega\cdot cm)^{-1}$, respectively.

Introduction

Interest in Prussian blue and several of its transition metal analogues has grown considerably in the past decade.[1-4] The diameter of interlattice channels in some cyanoferrates, determined by x-ray analysis, is ≈3.8 A[5] which is regarded as a class D molecular sieves. The fundamental reactions of these transition metal hexacyanometallates are still not fully understood even though a number of reports have been investigated.[6-8] Further studies are required to consider kinetic factors, of ion and electron diffusion and migration, and voltammetric factors of the shape and peak separation. These materials have been considered for practical applications such as electrochromic devices[9-11] electro-optical devices,[12,13] high reversible batteries,[14-16] ion-selective electrodes,[17-19] and as electrocatalysts.[20-22] Silver ferricyanide (SF), the highly insoluble polymeric form, is well-known. It is the silver analogue of Prussian blue consisting of a basic face centered-cubic polymeric network. Some cations will be penetrated into the lattice which is one of the characteristics of transition metal hexacyanide films. The ion transport within thin film might be closely related to electrostatic factors and ion polarizabilities. The color of these films are orange. Thin films of silver ferricyanide are shown to be electrochromic. In a previous report we have considered the kinetics of electrolysis of silver ferricyanide film.[23] In this report we are primarily concerned with the unsymmetry of SF thin films on a various supporting electrolytes. One of the essential goals of this research was to study the rate of electron transfer of a simple redox couple at the interface with the silver ferricyanide films. The electrode kinetics of the $Fe(CN)_6^{3-/4-}$ on silver ferricyanide were studied using a rotating platinum disc electrode. Surprisingly, the formation of Prussian blue is observed in 10^{-3} M Fe^{2+}/Fe^{3+} solution. The electronic conductivities have been made on bulk samples consisting of powdered silver ferricyanide pressed between inserting conducting electrodes.

Experimental

All chemicals used were reagent grade. Triply distilled water was used throughout. Voltammetric measurements were carried out in a glass cell with a three electrode configuration on a PAR Model 273 potentiostat. The electrodes were polished with an alumina suspension (0.3 micron) and cleaned in an equal-volume mixtures of concentrated sulfuric and nitric acid. The cleaned and polished electrodes were 5 cm lengths and 1 mm in a diameter of Pt wires. The rotating disc electrode (RDE) was first polished with an alumina powder (0.3 micron) on a polishing cloth attached a glass plate and rinsed thoroughly in an ultrasonic bath. The RDE was inserted in a 0.5 M H_2SO_4 for electrochemical pretreatment. The auxiliary electrode was a Pt wire and saturated calomel electrode (SCE) was used as a reference electrode. All potentials were recorded *vs* SCE. All solutions were deoxygenated for the electrochemical experiments.

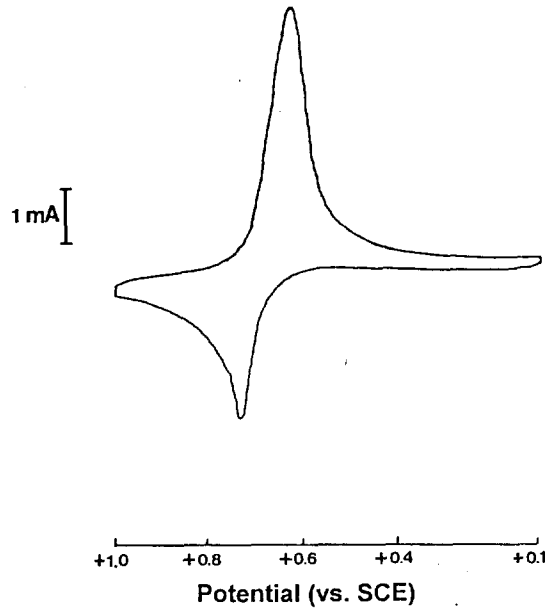

Figure 1. Voltammogram of 76 nm film of silver ferricyanide on a Pt disc electrode in 1.0 M KNO_3 solution; scan rate was 50 mV/s.

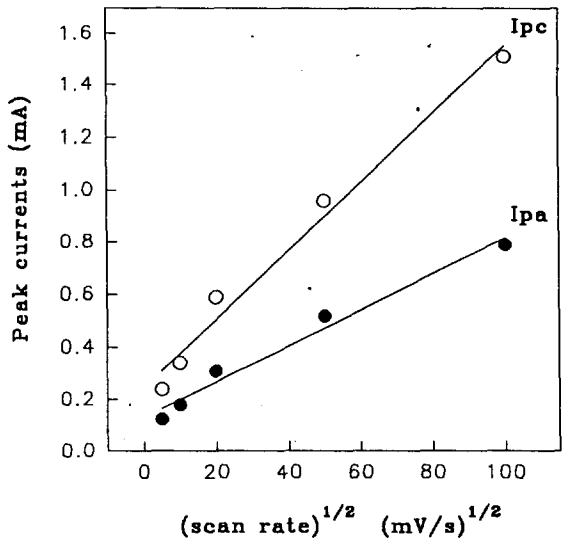

Figure 2. Peak current *vs.* the square root of the scan rate for a SF film on a Pt disc electrode in 1.0 M KNO_3 solution.

Thin silver films at the Pt electrodes were prepared by applying at −0.1 V for 1 min in presence of acidic 0.1 M $AgNO_3$. Silver ferricyanide thin films were obtained by holding the silver-plated Pt wires at 1.0 V *vs* SCE, in 0.1 $K_3Fe(CN)_6$ for 2 min. In the formation of silver ferricyanide, it should be carefully carried out the process of the thin silver film anodizing in the presence of ferricyanide. The film thickness, estimated from the total charge for the reduction, ranged from 50 to 100 nm. Infrared spectra of SF bulks were obtained with a NaCl cell by Nicolet 740 FT-IR spectrometer. The bulk samples were dried in a vacuum desiccator before the recording of the spectra. The RDE was constructed in our laboratory. The RDE was placed vertically in a solution and stirred by a variable speed motor controlled in the range of 1,000-7,000 rpm. The rotation speeds were continuously changed until the currents achieved stationary currents. The electron transfer rate constants are determined by measuring the observed current as a function of the rotation velocity.[24] The potassium rich SF bulk samples were prepared as follows: 50 m*l* of 0.01 M $AgNO_3$ solution was transferred into the equal volume of 0.1 M $K_3Fe(CN)_6$ and 0.1 M KNO_3 mixture solution. After centrifuged, and these compounds were dried under a vacuum desiccator. Potassium deficient compounds were obtained from the solutions of 0.01 M $K_3Fe(CN)_6$ transferred into the 0.1 M $AgNO_3$ solution.

Results and Discussion

The voltammogram of silver ferricyanide (SF) in 1.0 M neutral KNO_3 solution is shown in Figure 1. The mid-peak potential between cathodic and anodic peaks in 1.0 M KNO_3 solution is found to be 0.739 V. This voltammogram showed a similar feature to those observed for most of the transition metal hexacyanometallates, such as copper,[25] nickel,[26] zinc,[27] and chronium.[28] We also observed this asymmetry of the oxidation compared to the reduction wave under other conditions of the supporting electrolyte, such as pH 0, pH 2, and saturated O_2. An entirely similar voltammogram is obtained with platinum and gold wire electrodes, indicating no specific interaction between the silver ferricyanide films and the metal atoms. In the range between 1 and 100 mV/s, the peak current roughly dependence on the square root of the scan rate for oxidation and reduction processes is shown in Figure 2. This dependence suggests that both peak currents may be mainly affected by the diffusion of potassium ions although the details of electron transfer processes are not well understood and are currently being studied in the polymer film.[8,29] Further evidence for the role of potassium ion is obtained for voltammograms determined at different potassium ion concentrations. As a result, the Nernst slope was 55 mV/decade. In the electrocatalytic effects of group I cations and ammonium ion, all cations, except Li^+ and Na^+, were allowed to enter and leave the films. These cations transport may be closely related to the hydrated ionic radius and the crystal lattice size of SF and other transition metal hexacyanometallates.[6] The migration of ions into or out effects the viscoelastic properties of the electoactive polymer films which, in turn, effects the frequency of a quartz crystal microbalance (QCM)[30-32] so that the QCM will detect the transport of ions into or out of the films.

Two experimental procedures have been used in order to characterize the kinetics. There was voltammetry at relatively low scan rates and the RDE study. We have a metal electrode on which has been deposited a film containing donor R′ or acceptor Ox′ ions. In SF these ions may be chosen the Fe^{2+}/Fe^{3+} or $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couples because they fit so-called outer sphere electron transfer. In case of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couples, it is found that the voltammogram for a given couple on the modified film electrode was very similar to those obtained for the same couple on the bare metal electrode. From this, one could draw the conclusion that the film is not catalytic but is behaving as a single electron transport medium (*i.e.* like a metal). When the rate of the

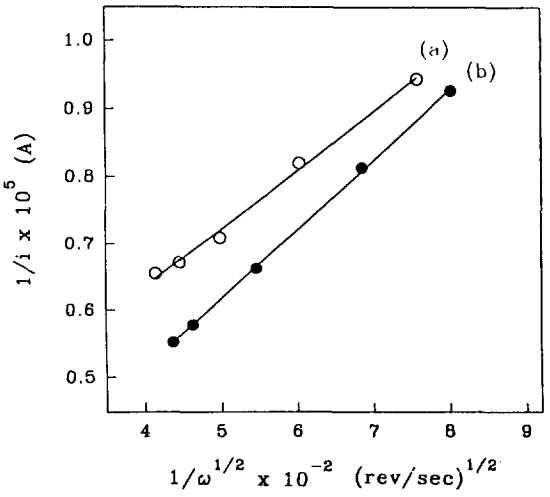

Figure 3. A plot of $1/i$ *vs* $1/\omega^{1/2}$ obtained for both (a) SF thin film and (b) bare Pt disc in 10^{-3} M $Fe(CN)_6^{-3/-4}$.

reaction is controlled both the diffusion and by the electron transfer, the electron transfer constants are determined experimentally by measuring the observed current as a function of the rotation velocity.[24] A plot of $1/i$ *vs* $1/\omega^{1/2}$, shown in Figure 3, yields the electron transfer rate constant. The Levich equation breaks down under the conditions of non-laminar flow. This means that rotation speeds must be kept below approximately 7000 rpm. After considered the effect of the geometry and ratio of disc to electrode diameter,[33,34] 1 mm diameter disc were selected to obtain these type of measurement in this work. The standard heterogeneous electron-transfer rate constants for SF films and bare electrode were 0.49×10^{-2} cm/s and 1.30×10^{-2} cm/s, respectively. The rate constant of electron transfer obtained with SF thin films is slightly less than that obtained for the same reaction on bare Pt electrode. The rate constant obtained on the bare Pt disc electrode is same order of magnitude compared to that reported.[35] Rough D_o values, evaluated from the slope of the plot of $1/i$ *vs* $1/\omega^{1/2}$, for $Fe(CN)_6^{3-/4-}$ at both SF thin film and a bare Pt disc electrode, are given 1.21×10^{-6} and 0.94×10^{-6} cm^2/s, respectively and the value obtained at a bare Pt disc electrode seems reasonable compared to that in the published paper.[36] Since we estimate an experimental error of ± 5% we may conclude that the redox electron transfer rate is essentially indifferent to whether the electrode is a SF film or whether it is a bare metal. On the other hands, these films were placed in 10^{-3} M Fe^{+2}/Fe^{+3} solution for some mins, we observed that orange color of the films was gradually changed into blue color. After taking these blue films out in the solution, we obtained a cyclic voltammogram using these blue film. As a result, the mid-peak potential is very close to that of Prussian blue. This phenomenon may be due to the result from the intercation exchange between silver and iron. Although it is not clear why this process is going on as yet, it might be closely related on the thermodynamic terms occurred by the composition variables of those films. The infrared spectra both potassium rich compound and potassium deficient compound could be obtained with a NaCl cell. The single sharp CN absorption bands are given at 2170 and 2094 cm^{-1}, respectively. Higher wavenumbers of CN stretch for the trasnsition metal hexacyanides are established to the higher oxidation state.[37] These wavenumbers are very close to those obtained from SF thin films before and after electrochemical treatment.[19] The conductivities, as determined from the slops of the i-V curves for a *ca.* 1 mm sample of dry SF powdered pressed between graphite electrodes, are 9.34×10^{-9} $(\Omega\cdot cm)^{-1}$ for potassium rich compound and 5.80×10^{-9} $(\Omega\cdot cm)^{-1}$ for potassium deficient compound, respectively. We have known that the conductivity for bulks depend on the potassium ion contents.

References

1. (a) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135. (b) Murray, R. W. *Electroanalytical Chemistry*; Bard, A. J. Ed.; Dekker: New York. 1984, Vol 13, p 191.
2. Bard, A. J. *J. Phys. Chem.* **1982**, *86*, 172.
3. Heller, A. *Acc. Chem. Res.* **1981**, *14*, 154.
4. Faulker, L. R. *Chem. Eng. News* **1984**, *14*, 28.
5. Nikolina, V. Ya.; Neimark, I. E.; Pointkovskaya, M. A. *Russ. Chem.* **1960**, 509.
6. Itaya, K.; Uchida, I.; Neff, V. D. *Acc. Chem. Res.* **1986**, *19*, 162.
7. Itaya, K.; Uchida, I.; Toshima, S.; *J. Electrochem. Soc.* **1982**, *129*, 1498.
8. Ellis, D.; Eckhoff, M.; Neff, V. D. *J. Phys. Chem.* **1981**, *85*, 1225.
9. Itaya, K.; Takahashi, S.; Toshima, S. *J. Appl. Phys.* **1982**, *53*, 804.
10. Carpenter, M. K.; Conell, R. S. *J. Electrochem. Soc.* **1990**, *137*, 2464.
11. Habib, M. A.; Maheswari, S. P.; Carpenter, M. K. *J. Appl. Electrochem.* **1991**, *21*, 203.
12. Deberry, D. W.; Viehbeck, A. *J. Electrochem. Soc.* **1985**, *132*, 1369.
13. Deberry, D. W.; Viehbeck, A. *J. Electrochem. Soc.* **1983**, *130*, 2439.
14. Neff, V. D. *J. Electrochem. Soc.* **1985**, *132*, 1382.
15. Messina, R.; Perichon, J. *J. Appl. Electrochem.* **1980**, *10*, 655.
16. Kaneko, M. *J. Polymer Sci. Polymer Lett.* **1986**, *24*, 435.
17. Engel, D.; Grabner, E. W. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 982.
18. Krishnan, V.; Xidis, A. L.; Neff, V. D. *Anal. Chim. Acta* **1990**, *239*, 7.
19. Gao, Z.; Zhou, X.; Wang, G.; Li, R.; Zhao, Z. *Anal. Chim. Acta* **1991**, *244*, 39.
20. Itaya, K.; Shoji, N.; Uchide, I. *J. Am. Chem. Soc.* **1984**, *106*, 3423.
21. Cox, J.; Kulesza, P. *Anal. Chem.* **1984**, *56*, 1021.
22. Li, F.; Dong, S. *Electrochim. Acta* **1987**, *32*, 1511.
23. Moon, S. B.; Xidis, A.; Neff, V. D. *J. Phys. Chem.* **1993**, *97*, 1634.
24. Bard, A. J.; Faulkner, L. R. *Electrochemical Method*; John-Wiley & Sons: New York, 1980.
25. Siperko, L.; Kuwana, T. *J. Electrochem. Soc.* **1983**, *130*, 396.
26. Bocarsly, A. B.; Sinha, S. *J. Electroanal. Chem.* **1982**, *140*, 167.
27. Rosseinsky, D. R.; Slocombe, J. D.; Soutar, A. M.; Monk, P. M. S.; Gilde, A. *J. Electroanal. Chem.* **1990**, *287*, 389.

28. Jiang, M.; Zhou, X.; Zhao, Z. *J. Electroanal. Chem.* **1990**, *287*, 389.
29. Leidner, C. R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1606.
30. Feldman, B. J.; Melroy, O. R. *J. Electroanal. Chem.* **1987**, *234*, 213.
31. Orata, D.; Buttry, D. A. *J. Am. Chem. Soc.* **1987**, *109*, 3574.
32. Deakin, M. R.; Byrd, H. *Anal. Chem.* **1989**, *61*, 290.
33. Prater, K. B.; Adams, R. N. *Anal. Chem.* **1966**, *38*, 153.
34. Galus, Z.; Adams, R. N. *J. Phys. Chem.* **1963**, *67*, 86.
35. Kawiak, J.; Jedral, T.; Galus, Z. *J. Electroanal. Chem.* **1983**, *145*, 163.
36. Oyama, N.; Ohsaka, T.; Yamamoto, N.; Matsui, J.; Hatozaki, O. *J. Electroanal. Chem.* **1989**, *265*, 297.
37. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; John Wiley & Sons: New York, 4th Ed.

Determination of Trace Metals in Atmospheric Particulates by Ion Chromatography

Yong-Keun Lee*, Hak-Chul Kim†, and Dong Soo Lee

Department of Chemistry, Yonsei Universty, Seoul 120-749, Korea
Received June 15, 1994

A simple and fast ion chromatographic method is developed for the determination of transition metals such as Fe, Cu, Ni, Zn and Co in atmospheric particulates. The method involves acid digestion, on-column preconcentration, and subsequent ion chromatographic detection. The precision of the method is less than 3% RSD at parts per billion level for the matals studied. No significant interferences are observed. The results obtained with this method agree well with those by ICP-AES.

Introduction

Transition metals such as Fe, Cu, Ni, Zn and Co in atmospheric particulates have been determined because of their environmental toxicities toward human health.[1-3] Various methods[4-7] have thus far been used and each method has its own merits and weaknesses. In this paper, an IC Method was used for the first time.

Since late 1970s, many researchers have been actively involved in the simultaneous determination of transition metals by ion chromatography. Transition metal ions are particularly suited for spectrometric detection using post column reaction with reagents such as 4-(2-pyridylazo)resorcinol (PAR), arsenazo III or dithizone.[8-9] Alternatively, transition metal ions may be detected by electrochemical methods such as coulometry at controlled potential, conductivity measurement and amperometry using various designs of working mercury electrodes.[10-13] However, there have been few reports of appling ion chromatography for the determination of transition metals in real environmental samples. Recently, ion chromatography has been applied for the determination of Fe, Cu and Zn in rainwater.[14]

In this study, we applied ion chromatography to the determination of Fe, Cu, Ni, Zu and Co in atmospheric particulates. By employing on-column preconcentration we have lowered detection limit significantly and removed matrix interferences.

†Present Address, Doosan Technical Center, 39-3, Songbok-Ri, Suji-Myon, Yongin-Gun, Kyonggi-Do 449-840, Korea

Experimental

Reagent and Apparatus. A Dionex 4000i ion chromatograph equipped with Dionex HPIC-CG5 concentration column (4×50 mn), HPIC-CS5 analytical column (4×250 mn) and 0.5 m*l* sample loop was used in this study. Most experiments were performed with an eluent of 6 mM pyridine-2,6-dicarboxylic acid (PDCA, Tokyo Kasei) at a pump rate of 1.0 m*l*/min. Eluent pH was adjusted to 4.6 with sodium acetate and acetic acid. A JAI model UV-detector 3702AB and a Hitachi model chromatointegrator D-2000 were used for data collection.

Atmospheric particulates were collected using a Kimoto model HV-121FT high volume air sampler. Labtam model UV-20, inductively coupled plasma atomic emission spectrometer was used for elemental analysis.

All solutions in this work were prepared with deionized water from Milli-Q system (Millipore Co.). HNO_3 and HF used for acid digestion were redistilled in Teflon still. 0.0125 % 4-(2-pyridylazo)resorconol (PAR) solution (Dotite) was prepared with 3 M NH_4OH and 1 M acetic acid. A11 other reagents were of reagent grade.

Multielement standard solutions were prepared by successive dilution of commercial 1,000 μg/m*l* atomic absorption standards (J. T. Baker). Certified reference materials (SRM) for urban particulate matters (NIST SRM-1648, U. S. A.) and vehicle exhaust particulate (NIES SRM-8, Japan) were analyzed for evaluating accuracy.

Particulate Collection and Dissolution. Atmospheric particulates were collected using a high volume sampler