Flow Injective Determination of Thiourea by Amperometry

Joon-Woo Lee, Sun-Il Mho[†], Chong Hong Pyun[‡], and In-Hyeong Yeo*

Department of Chemistry, Dongguk University, Seoul 100-715, Korea
[†]Department of Chemistry, Ajou University, Suwon 440-749, Korea
[‡]Division of Applied Science, KIST, Seoul 136-791, Korea
Received March 24, 1994

The amperometric responses of thiourea were studied in 0.1 M NaOH by flow injection analysis. D. C. amperometric and pulsed amperometric detection methods were applied for the determination of thiourea at novel metal electrodes such as Pt and Au. Triple-step potential waveforms were adopted in the pulsed amperometric detection. With an optimized pulsed waveform, the current for the oxidation of thiourea was examined with the variation of flow rate of carrier solution and with the change in the amount of sample injected. Gold working electrode turned out to be better in sensitivity and signal to noise ratio than Pt electrode in the pulsed amperometric detection of thiourea. Detection limit is estimated to be 5.33×10^{-5} M with this detection method.

Introduction

Flow Injection Analysis (FIA) introduced by Ruzicka and Hansen in 1975 can be easily automated to allow a rapid determination of a large number of analytes continuously in a short time.[1,2] A liquid sample is introduced into an unsegmented continuous flowing carrier system. The sample, then, is dispersed in carrier stream to form a sample zone. The concentration distribution of the sample zone is determined selectively at a detector depending on the characteristics of the analytes and on the selected detection methods. Spectroscopy and electrochemistry are the ones which are widely used in the detection schemes employed in the FIA. However, conventional spectrophotometric methods are not applicable without prior chemical derivatization for many aliphatic compounds which do not absorb strongly in the UV-visible region of electromagnetic wave.[3] Hence, electrochemical methods are better for those molecules. Among electrochemical detection methods, amperometry is widely used for its sensitivity.[4]

Thiourea and its derivatives have been received considerable attention because of their usages in agriculture, industry and medicine.[5,6] Therefore, various methods such as Raman spectroscopy,[7] stripping voltammetry,[8] potentiometry,[9] spectrophotometry,[10] titrimetry[11] have been suggested for the determination of thiourea. Voltammetric responces of thiourea have been investigated at noble metal electrodes.[12-14]

In this work, we assembled a FIA system and tested its performance with amperometric determination of thiourea as a representative analyte of organosulfur compounds. Our work was focused on analyzing thiourea in alkaline solution with the FIA system. Changes of peak heights and widths with flow rates, amounts of sample injected, and concentrations of thiourea were studied. Also, dc amperometry and pulsed amperometry were applied to the analysis of thiourea for the comparison of the two methods.

Experimental

Instruments.   A schematic diagram of the FIA system
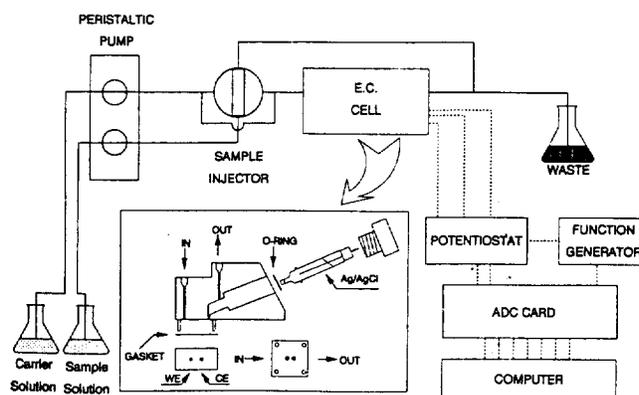
Figure 1. Schematic diagram of a flow injection analysis set-up.

is shown in Figure 1. A peristaltic pump (Gilson Inst., model miniplus 2) was used to control the flow rate of carrier streams and samples. The pump consisted of four channels with the digital setting of a speed potentiometer. Two silicone tubes (id : 1.52 mm) for the carrier solution and a sample were positioned around the rollers located in the head of the pump. The tubes were kept in place with the plastic stops. The relationship between flow rates and the digital settings was calibrated with the carrier solution so that flow rates of the solution could exactly be known. Injections of samples were made with a sample injector (Rheodyne, model 50, 4 way type) mounted on an pneumatic actuator (Rheodyne, model 5701). The actuator permitted automatic operation of swiching between load and inject positions by nitrogen gas. The minimum pressure of nitrogen to switch the positions was greater than 60 psi in our system. A thin layer electrochemical cell of three-electrode was used; one of the electrode in dual Pt electrodes (EG & G. model MP 1303) or in dual Au electrodes (EG & G. model MP 1302), which were insulated with Kel-F except the electrode surface, was used as a working electrode. An Ag/AgCl electrode (EG&G. Cat. No. 21905 E) was used as a reference electrode and the other electrode in the dual Pt or Au electrodes as a counter electrode. The surface of the working electrode was polished with 0.05 μm γ-Alumina and washed with a fresh por-

Flow Injective Determination of Thiourea

Bull. Korean Chem. Soc. **1994**, Vol. 15, No. 12 1039

Table 1. Triple-step potential waveforms

	Platinum electrode		Gold electrode	
	Potenaial (mV)	Duration time (msec)	Potential (mV)	Duration time (msec)
Potential, E1	500	200	620	200
Potential, E2	1500	200	1500	200
Potential, E3	−600	600	−600	600

tion of water thoroughly. All electrode potentials were reported with respect to the Ag/AgCl electrode in this study. A potentiostat (Amel Co., model 553) and a function generator (Amel Co., model 568) were used to control potentials and measure currents. Recordings of currents and potentials were made with an IBM XT compatable computer through an interface card (Interactive Microware Inc., Adalab-PC).

Reagents. All chemicals were analytical reagent grade and were used without further purification. The supporting electrolyte was 0.1 M NaOH for all experiments. All solutions were made with purified water obtained by the Milli-Q purification system. Thiourea (Shinyo Pure Chemical Co., 95%) was used as received.

Software. A program to control the interface card was written in Basic A (Microsoft Inc.). The experimental data from the interface card were treated with a program written in Turbo Pascal 5.0 (Boland Inc.) and Lotus 123 release 2A (Lotus Development).

Electrochemical measurements. Detection potentials were chosen from cyclic voltammograms obtained at gold and platinum working electrodes in 0.1 M NaOH solution with and without thiourea. Currents were sampled continuously when the detection potentials were applid to the working electrode for dc amperometry. For pulsed amperometry, a pulsed waveform was kept applying to the working electrode when the analyte flew through the electrochemical cell. The pulsed waveform consisted of three steps; detection potential E_1, oxidation potential E_2, and adsorption potential E_3. E_2 was usually more anodic than E_1. At this potential, potential was high enough to form a higher valance state of oxides. Hence, the adsorbed oxidation products were desorbed oxidatively to clean electrode surface. Adsorption potential, E_3, was a negative potential at which the analyte was adsorbed at the surface of the electrode.

When the analyte is flowing through the electrochemical cell, potentials of E_1, E_2, and E_3 are cycled and kept applying to the working electrode. Faradaic current is sampled at the last 20 msec during the detection potential period (180 msec after the start of the detection potential), where the charging current is decayed away. Triple-step pulse potentials and duration times at those potentials are listed in Table 1. Various parameters such as flow rate, amounts of analyte injected, and pulsed waveforms are changed to monitor the magnitude and shape of the peak current sampled at the detection potential.

Results and Discussion

The current potential responses shown in Figure 2 were obtained in the electrochemical cell without purging the solu-
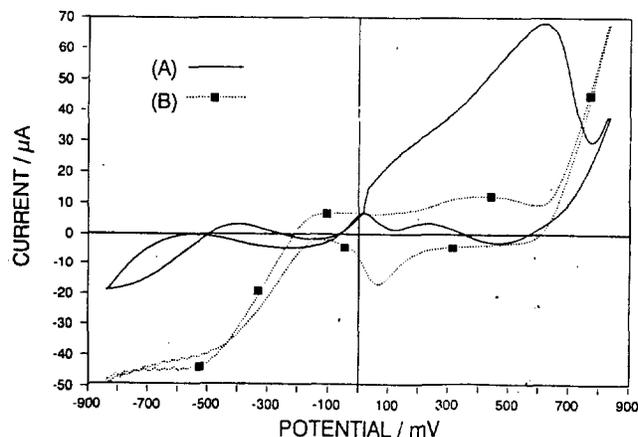

Figure 2. Current-voltage curves of thiourea at a Au electrode in 0.1 M NaOH. scan rate: 50 mV/sec, flow rate: 1.4 mL/min., concentration: (A) 1×10^{-4} M; (B) 0.00 M.
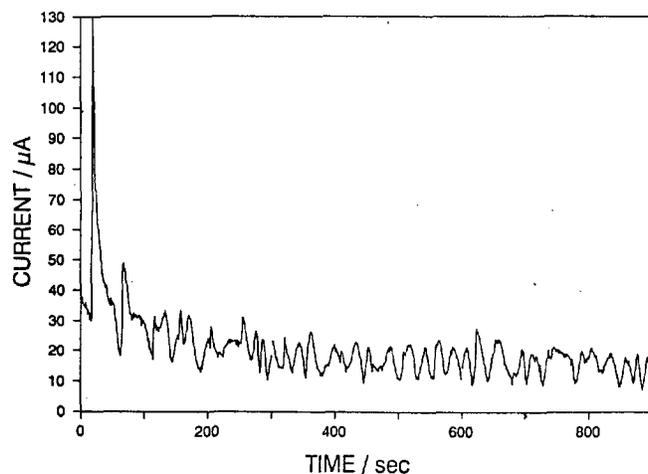
Figure 3. Amperometric response for successive injections of 1×10^{-3} M thiourea at platinum electrode in 0.1 M NaOH with a constant potential of 500 mV. flow rate: 2.3 mL/min. volume of sample loop: 0.1 mL.

tion with nitrogen gas. For the residual $i-E$ curves, formation of gold oxides occurred at $E > ca.$ 300 mV was followed by the evolution of oxygen at $E > ca.$ 700 mV in the positive potential scan. Reduction of gold oxides was observed with the peak current at about 50 mV followed by reduction of the dissolved oxygen at below −200 mV in the negative scan. In the presence of thiourea, a large and broad peak was observed in the positive potential scan. This peak was interpreted as a one electron oxidation of sulfur atom in thiourea and subsequent dimerization to form formamidine disulfide.[15,16] Also, further oxidation of thiourea could produce sulfate, which was confirmed by forming white precipitates after addition of Ba^{2+} following extensive oxidation.[14] For the negative scan, the current was largely suppressed in the potential range for the reducton of oxygen. It can be deduced that the adsorption of thiourea itself or oxidation products formed in the positive scan prohibit the reduction of oxygen.

For the analysis of thiourea, a detection potential has to be determined for each working electrode. From the $i-E$
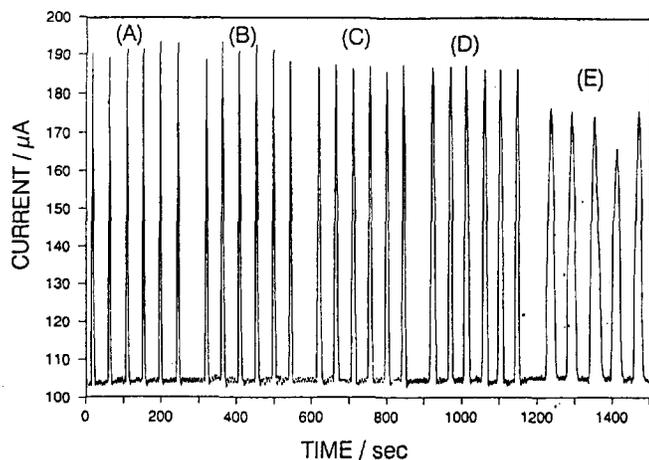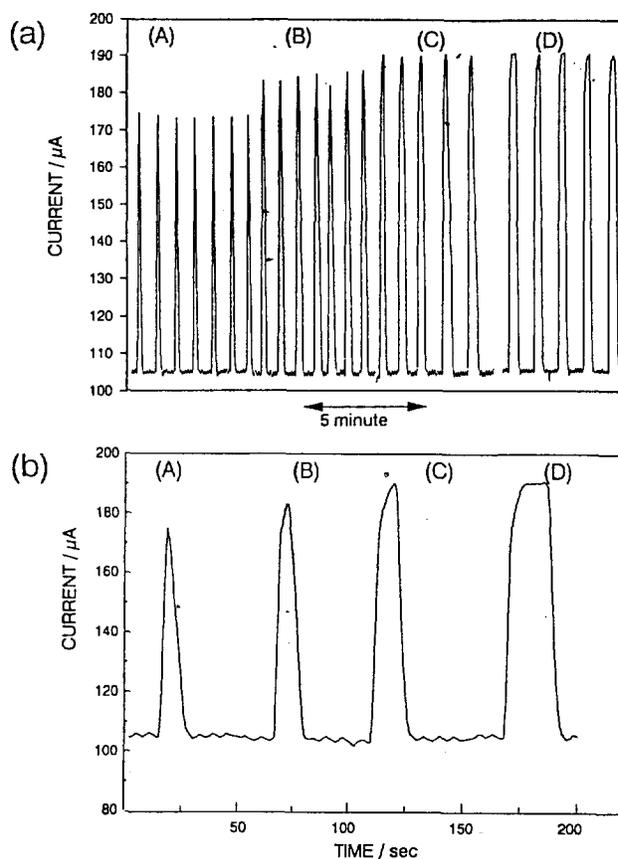
Figure 4. Variation of peak current for the detection of 5.0×10^{-4} M thiourea at an Au working electrode with different flow rates of carrier solution by pulsed amperometry; E_1: 620 mV (200 msec), E_2: 1500 mV (200 msec), E_3: -600 mV (600 msec), flow rate: (A) 3.8 mL/min, (B) 3.0 mL/min, (C) 2.3 mL/min, (D) 1.4 mL/min, (E) 0.8 mL/min; volume of sample loop: 0.1 mL.

curves of 1.0×10^{-4} M of thiourea at a gold working electrode in 0.1 M NaOH, the detection potential was 620 mV (Figure 2), where the current difference between sample and blank solutions was maximum. The same experiment was run for a Pt working electrode and the detection potential was chosen to be 500 mV. Therefore, currents were sampled with the potentials of 620 mV and 500 mV applying at the Au and Pt electrodes, respectively.

While applying the constant potential of 500 mV at the Pt electrode, a constant concentration of 1.0×10^{-3} M thiourea in 0.1 M NaOH solution was injected continuously with a constant time interval. A plot of measured currents *vs.* time is shown in Figure 3. At the first injection of thiourea, a large current was observed initially and the current decreased drastically. Even with successive injections, the measured current is very small and it is hard to differentiate from the resisual current. When the Au electrode was used as a working electrode, a simillar phenomenon was observed; reproducible peak currents could not be obtained. Oxidation products formed at the electrode are considered to be adsorbed to the electrode surface or interact with the electrode surface, which results in deactivation of the electrode with time. Hence, the decrease in current is resulted.

To get a reproducible signal with time the electrode surfaces should be cleaned periodically by potential pulse or by mechanically polishing the electrode surfaces.[17,18] With pulsed amperometry,[19,20] applying far positive and far negative potentials in each cycle at the electrode polarizes the electrode to renew the electrode surface, which results in very reproducible current shape and magnitude. Also, sampling current at the last few milliseconds during the detection potential prohibits the double layer charging current from overlapping with the signal, which causes an enhanced signal to noise ratio.

The Au electrode gives larger current for oxidation of thiourea than the Pt electrode. Hence, the gold working electrode was used to determine the optimum conditions of flow


Figure 5. (a) Change of peak current shape for the detection of 5.0×10^{-4} M thiourea at an Au working electrode with the volume of sample injected by pulsed amperometry; E_1: 620 mV (200 msec), E_2: 1500 mV (200 msec), E_3: -600 mV (600 msec), flow rate: 1.4 mL/min., volume of sample loop: (A) 0.05 mL, (B) 0.1 mL, (C) 0.25 mL, (D) 0.5 mL. (b) Enlargement of the shape of peak current in (a).

rate of carrier solution, amount of sample injection, and potential waveform adopted. The reason of larger current being observed in the Au electrode is that thiourea in aqueous solution is likely to react with gold to form stable cationic complexes.[16]

$$Au + 2CS(NH_2)_2 \rightarrow Au[CS(NH_2)_2]_2^+ + e$$
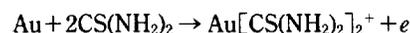
With an optimized pulsed waveform, currents for oxidation of 5.0×10^{-4} M thiourea at the Au working electrode as a function of flow rate of the carrier stream are shown in Figure 4. The magnitude of current increases as the flow rate increases. This could be explained by a relationship between the limiting current and the thickness of diffusion layer. According to the Cottrell equation,[21] diffusion limited current is inversely proportional to diffusion layer thickness, which is also inversely proportional to the flow rate. Hence, increased flow rate results in a thinner diffusion layer, which gives us increased diffusion current. It is our observation that significant enhancement in current signal does not occur with the flow rate greater than 2.0 mL/min.

Shown in Figure 5a are oxidation currents of 5.0×10^{-4} M thiourea by pulse amperometry with different amounts of sample injected. As the volume of sample loop is increa-

Flow Injective Determination of Thiourea

Bull. Korean Chem. Soc. **1994**, Vol. 15, No. 12 1041
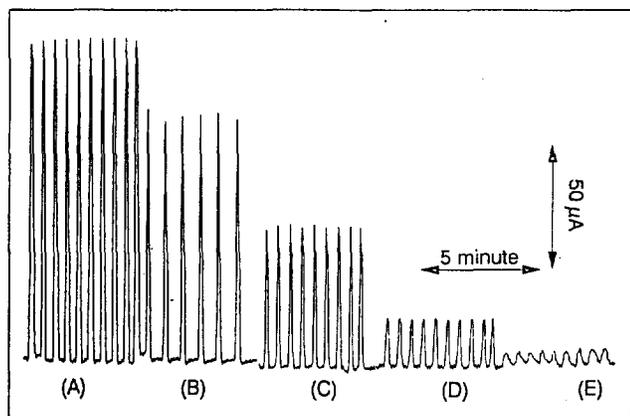
Figure 6. Representitive peak currents for different concentrations of thiourea in 0.1 M NaOH at an Au electrode by pulsed amperometry; E_1: 620 mV (200 msec), E_2: 1500 mV (200 msec), E_3: −600 mV (600 msec); flow rate: 2.3 mL/min, concentration of thiourea: (A) 1.0×10^{-3} M, (B) 5.0×10^{-4} M, (C) 2.0×10^{-4} M, (D) 1.0×10^{-4} M, (E) 5.0×10^{-5} M.

Figure 7. A plot of peak current response as a function of thiourea concentration in 0.1 M NaOH.

sed, the peak current increases and the widths of the peak are widened. It clearly shows in Figure 5b that oxidation of analyte at the electrode surface cannot reach a steady state with smaller sample amounts, which results in a smaller, sharp peak current. On the other hand, with larger amounts of sample injected, oxidation at the electrode surface reaches a steady state and the current peak broadens out at the maximum constant value.

The distance between the injection port and detection cell affects the peak shape of current. The width of peak current becomes wider and the peak height decreases as the distance increases because greater dispersion of analyte might occur in the carrier stream for the larger distance to flow. Hence, the shorter the distance between the injection port and the detector, the better results can be obtained. The distance between the injector and the detector is 17.8 cm of 0.33 mm inside diameter in our system. The time flowing through the tube is approximatly 0.65 sec with a flow rate of 1.4 mL/min. Because it takes at least 25 seconds for one sample to be passed in the electrochemical detetor, it is considered that our tubing size does not cause a severe peak broadening.

Shown in Figure 6 is the concentration dependence of current with a constant carrier flow velocity and with a constant volume of sample loop. The magnitude of current increases as the concentration of thiourea increases (Figure 7). With an optimum condition for the analysis of thiourea, concentration dependence of current was observed in the concentration range of 5.0×10^{-5} M-1.0×10^{-3} M of thiourea. The anodic response of thiourea is expected to be strongly influenced by its adsorption isotherm, because the mechanism for anodic detection of sulfur compounds is believed to involve adsorption *via* sulfur atoms onto oxide-free metal atoms in the electrode surface.[14] Anodic detection of adsorbed sulfur compounds occurs during anodic formation of oxide on noble metal electrodes with concomitant oxidative desorption of sulfur species. Because preadsorption is a necessary step in the detection of sulfur compounds,[14] severe
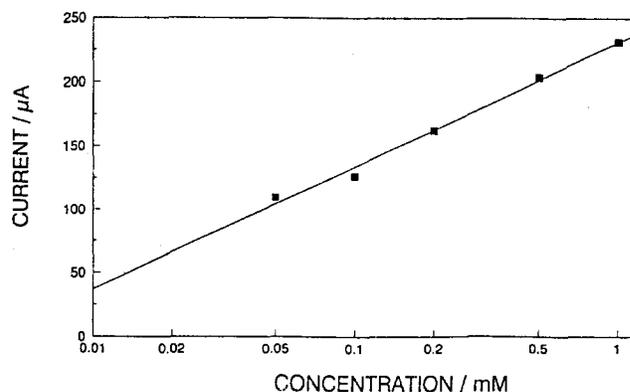
negative deviations from linearity for highly concentrated solutions are expected. We also observe the nonlinearity of current *vs.* concentration as the concentration of sample increases.

Therefore, the linear response shown in Figure 7 is obtained by plotting currents with concentrations in log scale. The detection limit of 5.33×10^{-5} M is estimated with these experimental conditions, where S/N is 3.

In conclusion, pulse amperometric detection of thiourea in FIA gives better reproducible detection currents compared with dc amperometric detection. Also, the Au electrode gives better results than the Pt electrode. A lower detection limit will be able to be obtained with an optimized pulsed waveform and duration time. Further investigation is in progress.

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Electrochemical Behavior of the Reduction of Thin Films of Ag₃Fe(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} cm²/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.