

# Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 13. Detection of Aqueous Iron by in Situ Complexation with 2,2'-Bipyridine

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**A spectroelectrochemical sensor with attenuated total reflectance at an indium-doped tin oxide (ITO) optically transparent electrode coated with a thin film of Nafion has been demonstrated for the determination of aqueous iron ion. The novelty of this sensor stems from its ability to take up colorless iron ion ( $\text{Fe}^{2+}$ ) from solution and complex it with an organic ligand, 2,2'-bipyridine (bipy), that has been previously loaded in the optically transparent charge-selective Nafion film coating the electrode. The resulting complex ion, tris(2,2'-bipyridyl)iron(II),  $\text{Fe}(\text{bipy})_3^{2+}$ , absorbs strongly, making it easily detectable via optical spectroscopy.  $\text{Fe}(\text{bipy})_3^{2+}$  loaded into the selective film is oxidized to colorless  $\text{Fe}(\text{bipy})_3^{3+}$ , which gives rise to an absorbance change for quantifying iron. This paper maps the development of this sensor, from the spectroelectrochemical characterization of the complex ion at an ITO optically transparent electrode to an analysis of the uptake, retention, and optical response of the complex ion in the Nafion film. Finally, an evaluation of the uptake of aqueous  $\text{Fe}^{2+}$  by the bipy-loaded Nafion film is reported. These data include preliminary results illustrating the dependence of the sensor response on differing concentrations of  $\text{Fe}^{2+}$  in solution.**

The utility of coupling the traditional spectroelectrochemistry experiment with a charge-selective film on an electrode surface to form a sensor with three modes of selectivity has been demonstrated.<sup>1,2</sup> For a chemical species to be detected directly by such a spectroelectrochemical sensor, three requirements must be satisfied: (1) it must partition into a selective film, (2) it must be electrochemically oxidizable or reduceable at the underlying electrode, and (3) its oxidized and reduced forms must have different molar absorptivities at the wavelength of light chosen for analysis. Thus, the analytical signal is obtained by measuring

the change in absorbance ( $\Delta A$ ) between the two redox states in the preconcentration film in response to electrochemical modulation. Selectivity is enhanced by employing attenuated total reflectance (ATR) techniques rather than transmission since the evanescent wave of the probing radiation only penetrates into the region of the charge-selective film and not into the bulk solution where interfering chemical species may be present.

To date, sensor designs based on this concept have been developed to detect a variety of charged transition metal complex ions, notably  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Ru}(\text{bipy})_3^{2+}$ , where bipy = 2,2'-bipyridine, as well as others.<sup>1,2</sup> Work has also been done to investigate and improve the properties of the optically transparent polymeric cation and anion exchange films into which analyte ions partition,<sup>3–5</sup> as well as to improve detection limits by employing signal averaging<sup>6</sup> and planar waveguide technology.<sup>7,8</sup> The effectiveness of different potential modulation waveforms (e.g., triangular vs potential step) has been examined,<sup>9</sup> along with sensor response to analyte solutions in the presence of chemical interferences.<sup>2</sup> An optimized sensor for detection of ferrocyanide has found application in remediation of nuclear waste stored in underground tanks at the Hanford Site near Richland, WA.<sup>10</sup> An analyte with no visible absorbance in either oxidation state has been detected indirectly by its effect on the electromodulation of a mediator immobilized in the film.<sup>11</sup>

(1) Shi, Y.; Slaterbeck, A. F.; Seliskar, C. J.; Heineman, W. R. *Anal. Chem.* **1997**, *69*, 3679–3686.

(2) Shi, Y.; Seliskar, C. J.; Heineman, W. R. *Anal. Chem.* **1997**, *69*, 4819–4827.

(3) Shi, Y.; Seliskar, C. J. *Chem. Mater.* **1997**, *9*, 821–829.

(4) Gao, L.; Seliskar, C. J. *Chem. Mater.* **1998**, *10*, 2481–24189.

(5) Gao, L.; Seliskar, C. J.; Heineman, W. R. *Anal. Chem.* **1999**, *71*, 4061–4068.

(6) Slaterbeck, A. F.; Ridgway, T. H.; Seliskar, C. J.; Heineman, W. R. *Anal. Chem.* **1999**, *71*, 1196–1203.

(7) Ross, S. E.; Seliskar, C. J.; Heineman, W. R. *Anal. Chem.* **2000**, *72*, 5549–5555.

(8) Ross, S. E.; Seliskar, C. J.; Heineman, W. R.; Aryol, S.; Nevin, J. H. In *Chemical and Biological Sensors and Analytical Methods II*; Butler, M., Vanysek, P., Yamazoe, N., Eds.; The Electrochemical Society: Pennington, NJ, 2001; pp 499–510.

(9) Slaterbeck, A. F.; Stegemiller, M. L.; Seliskar, C. J.; Ridgway, T. H.; Heineman, W. R. *Anal. Chem.* **2000**, *72*, 5567–5575.

(10) Stegemiller, M. L.; Heineman, W. R.; Seliskar, C. J.; Ridgway, T. H.; Bryan, S. A.; Hubler, T. *Environ. Sci. Technol.*, submitted.

(11) DiVirgilio-Thomas, J. M.; Heineman, W. R.; Seliskar, C. J. *Anal. Chem.* **2000**, *72*, 3461–3467.

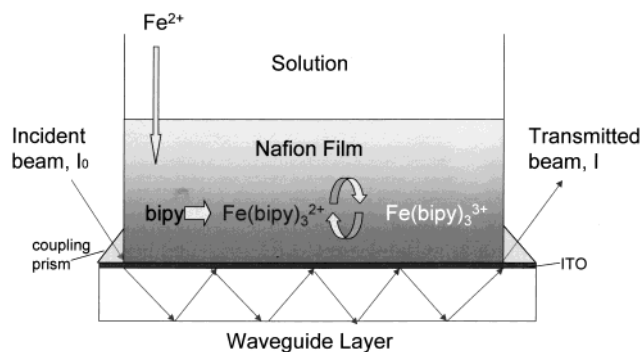


Figure 1. Schematic diagram of spectroelectrochemical sensor for  $\text{Fe}^{2+}$ .

Previously reported sensors have been shown to detect stable complexes in which only one oxidation state is strongly absorbing. This gives a large difference in molar absorptivity ( $\Delta\epsilon$ ) during electrochemical modulation between the two redox forms, which results in good sensitivity for the optical detection. However, none has yet been developed to sense free metal ions in which both oxidation states are only weakly absorbing, which gives only a small  $\Delta\epsilon$  during electrochemical modulation and poor sensitivity for the optical detection. Such a sensor would be invaluable in remote-sensing applications in which complex ions with desirable sensing properties do not occur under native conditions. In response to this need, we report herein a novel iron sensor that is sensitive to free iron ion in aqueous solution. We have developed this sensor by incorporating an organic ligand, 2,2-bipyridine (bipy), into the ion-selective film coating the electrode surface such that when aqueous  $\text{Fe}^{2+}$  partitions into the film, it also complexes with the preconcentrated bipy, resulting in a strongly absorbing complex ion,  $\text{Fe}(\text{bipy})_3^{2+}$ , that remains absorbed within the film. The analytical signal results from the absorbance difference brought on by electrochemical cycling between the absorbing reduced  $\text{Fe}(\text{bipy})_3^{2+}$  state and the colorless oxidized  $\text{Fe}(\text{bipy})_3^{3+}$  state of the complex ion. The concept of this sensor is illustrated in Figure 1. The detected signal should be proportional to the concentration of  $\text{Fe}(\text{bipy})_3^{2+}$  in the film, which is in turn proportional to the concentration of  $\text{Fe}^{2+}$  in bulk solution.

The goals of this paper are to (1) electrochemically and spectrally characterize  $\text{Fe}(\text{bipy})_3^{2+}$  at an indium-doped tin oxide (ITO) optically transparent electrode (OTE), (2) characterize the rate of uptake and subsequent stability of  $\text{Fe}(\text{bipy})_3^{2+}$  in the charge-selective film, (3) analyze the effects of preloading the charge-selective film with bipy ligand on the subsequent uptake and detection of free  $\text{Fe}^{2+}$  from aqueous solution, and (4) examine the concentration dependence of the sensor signal on the concentration of  $\text{Fe}^{2+}$  in pure, standard aqueous solutions.

## EXPERIMENTAL SECTION

**Materials.** The following chemicals were used: 1,10-phenanthroline (Aldrich), 2,2'-bipyridine (Baker), ferrous ammonium sulfate ( $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , Fisher), sodium chloride (Mallinckrodt), and Nafion (5% solution in lower aliphatic alcohols and 10% water, Aldrich). All reagents were used without further purification. Solutions containing complex ions were prepared by dissolving the appropriate amount of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  with a 4-fold excess of ligand into 0.1 M NaCl electrolyte solution

(prepared with distilled/deionized water from a Barnstead purification system); solutions for analysis of free  $\text{Fe}^{2+}$  were prepared in exactly the same manner, but without the ligand. ITO tin float glass (11–50  $\Omega/\square$ , 150-nm-thick ITO layer over tin float glass) was obtained from Thin Film Devices. This ITO tin float glass was cut into individual 1  $\times$  3 in. slides, scrubbed with Alconox, and rinsed thoroughly with deionized water and 1-propanol prior to use. The cleaned ITO glass slides were then stored in contact with air prior to use.

### Formation of Nafion Thin Films on ITO Glass Substrates.

Thin Nafion films were formed by spin-coating stock Nafion solution onto the ITO glass slides using a Headway spin-coater operated at 2000 rpm for 30 s. In this manner, film thicknesses of about 190–200 nm were routinely obtained. One (transmittance applications) or both (ATR applications) ends of the ITO side of the glass slide were masked with tape to a width of  $\sim 1$  cm prior to spin-coating, leaving these surfaces uncoated for electrical contact or prism coupling.

**Instrumentation.** Transmission spectroelectrochemistry measurements at normal incidence were acquired using a Spectral Instruments (model SI 400) CCD array UV–visible spectrometer and an EG&G PAR model 173 potentiostat/galvanostat, both under computer control. All data were acquired digitally, and subsequent data analysis and manipulation were accomplished using commercial spreadsheet and graphics algorithms.

ATR spectroelectrochemical measurements were made using an instrumental setup that has been previously described.<sup>1,2,12</sup> Briefly, the light source was a xenon arc lamp/monochromator (ILC Technology, model 302 UV). The arc lamp/monochromator provided a narrow wavelength range ( $\sim 10$  nm full width, half-maximum, fwhm) centered on the maximum absorbance of  $\text{Fe}(\text{bipy})_3^{2+}$ . Light from the source was focused onto the polished end of a 600- $\mu\text{m}$  silica step-index optical fiber (Fiberguide Superguide G, NA = 0.22) with a microscope objective positioned at the exit slit of the monochromator. The light from this fiber was coupled into the ITO glass slide of the spectroelectrochemical cell using a microscope objective and a Schott SF6 coupling prism (Karl Lambrecht, Chicago, IL). A high-viscosity refractive index standard fluid (Cargille,  $n = 1.59$ ) was used to span the prism/ITO glass gap. The angle of the incident light into the prism and the alignment of the cell were adjusted to maximize the ATR throughput, as determined by measuring the intensity of the decoupled light. Light propagating through the ITO glass slide was decoupled by using another SF6 coupling prism, and the emergent beam was focused through a microscope objective onto a simple photodiode detector (Photonic Detectors, Digi-Key PDB-V107). The signal from the detector was amplified with an op-amp follower with gain circuit and fed into a National Instruments A/D, D/A card (PCI-MIO-16E-4) for further processing. Data files were imported into commercial spreadsheet and graphics algorithms for data manipulation and plotting.

**Spectroelectrochemical Cells.** Transmission spectroelectrochemistry measurements at normal incidence were made using optically transparent thin-layer electrodes constructed using a 1  $\times$  3 cm ITO glass slide covered with a similarly sized glass microscope slide using previously published methods.<sup>13,14</sup> Contact

(12) Slaterbeck, A. F. Ph.D. Dissertation, University of Cincinnati, 1998.

(13) DeAngelis, T. P.; Heineman, W. R. *J. Chem. Educ.* **1976**, *53*, 9, 594–597.

was made to the electrode using a metal alligator clip. The solution reservoir was a small plastic Petri dish; the reference and auxiliary electrodes were BAS Ag/AgCl and a Pt wire, respectively.

ATR spectroelectrochemical measurements were performed using a plastic cell described previously.<sup>1,2</sup> Electrical contacts with the ITO glass slide were made with four copper clips attached to each exposed corner of the ITO glass. The reference electrode was a Cypress Systems, Inc. Ag/AgCl, and the auxiliary electrode was a platinum mesh.

## RESULTS AND DISCUSSION

**Choice of Chemical System.** To demonstrate the basic operation of this sensor, an appropriate chemical system was chosen for which several criteria had to be met: (1) The iron-containing complex ion must have different spectral characteristics between its different oxidation states so that one oxidation state absorbs much more strongly than the other at an accessible wavelength. (2) The complex ion should remain relatively stable in both of its oxidation states. (3) The complex ion must partition into the cation-selective film so that it can be preconcentrated there. (4) The complex ion couple must possess a redox potential that is accessible within the electrochemical potential window of the ITO electrode. (5) It is desirable that the complex ion exhibit facile, well-defined electrochemical behavior at the ITO electrode. (6) The chosen ligand must partition into and become preconcentrated in the ion exchange film.

Two cationic iron-containing complex ions were evaluated according to criteria 1–5 listed above, namely, tris(1,10 phenanthroline)iron(II) ion and  $\text{Fe}(\text{bipy})_3^{2+}$ . Both candidates easily satisfied all of the criteria except for the third: only  $\text{Fe}(\text{bipy})_3^{2+}$  partitioned readily into the cation-selective Nafion film. Therefore, all subsequent experimentation was with bipy as the coordinating ligand.  $\text{Fe}(\text{bipy})_3^{2+}$  absorbs strongly in the visible range ( $\lambda_{\text{max}} = 520 \text{ nm}$ ; molar absorptivity,  $86\,500 \text{ M}^{-1} \text{ cm}^{-1}$ ) whereas the oxidized form  $\text{Fe}(\text{bipy})_3^{3+}$  is colorless. The sensitivity of this sensor would be much greater than that for hydrated  $\text{Fe}^{2+}$  because of the much larger  $\Delta\epsilon$  ( $86\,500 \text{ M}^{-1} \text{ cm}^{-1}$ ) for electromodulation of  $\text{Fe}(\text{bipy})_3^{2+/3+}$  than for hydrated  $\text{Fe}^{2+/3+}$ , which has a small  $\epsilon$  in both oxidation states in the visible spectrum ( $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ :  $\epsilon < 1 \text{ M}^{-1} \text{ cm}^{-1}$  in visible range.<sup>15</sup>  $\text{Fe}^{3+}$ : the various hydroxo species, such as  $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ , are pale yellow because of charge-transfer bands in the UV that have tails extending into the visible range.<sup>16</sup>). Bipy forms strong complexes with both  $\text{Fe}^{2+}$  ( $\log K = 17.2$ ) and  $\text{Fe}^{3+}$  ( $\log K = 16.29$ ).<sup>17</sup>

**Spectroelectrochemical Characterization of  $\text{Fe}(\text{bipy})_3^{2+}$ .** During the evaluation effort, our first objective was to characterize the  $\text{Fe}(\text{bipy})_3^{2+/3+}$  couple as a spectroelectrochemical probe. Electrochemically,  $\text{Fe}(\text{bipy})_3^{2+}$  exhibited well-defined voltammetry at a bare ITO electrode; plots of both anodic and cathodic peak currents versus square root of potential sweep rates were linear (data not shown). Spectroelectrochemical behavior was determined using a traditional single-pass transmittance ITO optically transparent thin-layer electrode (OTTLE) with the incident beam

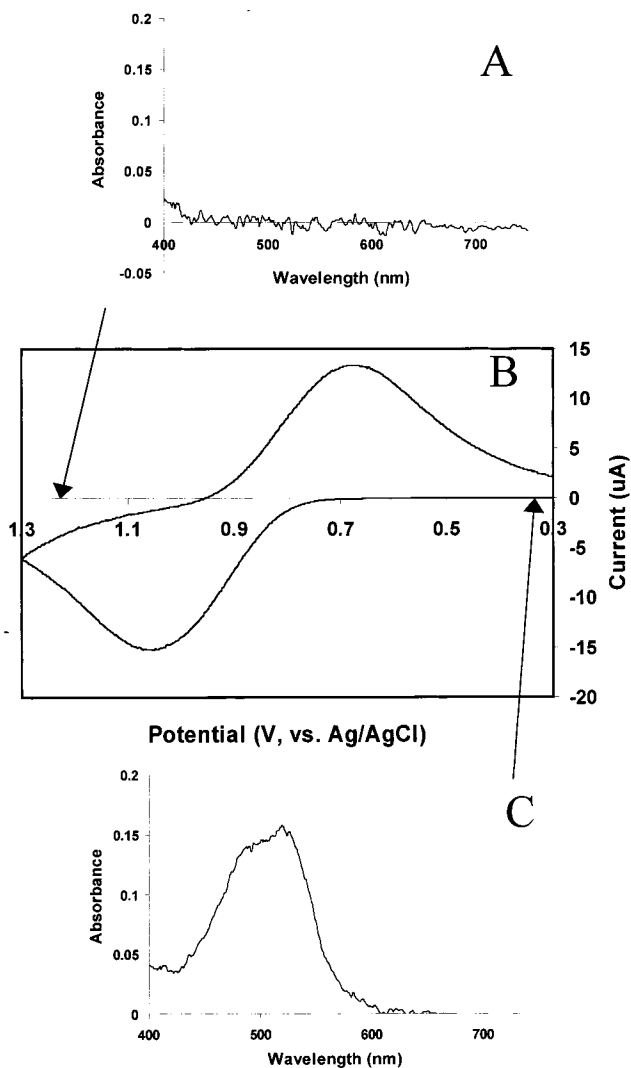


Figure 2. Panel B: cyclic voltammogram recorded with an ITO OTTLE; the voltammogram was recorded by cycling the OTTLE in an aqueous solution that was  $0.1 \text{ mM Fe}(\text{bipy})_3^{2+}$  and  $0.1 \text{ M NaCl}$ . Panel A: absorbance spectrum obtained at equilibrium after application of a potential step to  $1.010 \text{ V}$  (vs Ag/AgCl). Panel C: absorbance spectrum after application of a potential step to the negative limit of  $0.300 \text{ V}$  (vs Ag/AgCl).

normal to the electrode surface. Figure 2 illustrates a typical thin-layer voltammogram of  $0.1 \text{ mM Fe}(\text{bipy})_3^{2+}$  in aqueous  $0.1 \text{ M NaCl}$  acquired at a bare ITO OTTLE at a potential sweep rate of  $5 \text{ mV/s}$ . The voltammogram is well-defined with an  $E^{\circ} = 0.823 \text{ V}$  (vs Ag/AgCl). Panels A and C show the absorbance spectra of the fully oxidized and reduced states, respectively. It is apparent that the electrochemistry is accompanied by distinct changes in the optical signal; the oxidized state is transparent over the spectral region examined, whereas the reduced state absorbs strongly at  $520 \text{ nm}$ . Therefore, electrochemical modulation between these two oxidation states should lead to a well-defined absorbance change that can be monitored as the analytical signal.

To further characterize the probe spectroelectrochemically, a Nernst plot was obtained by applying potential steps to the ITO electrode and monitoring the absorbance once the system reached equilibrium. A spectroelectrochemical Nernst<sup>13</sup> plot of absorbance change versus potential exhibited good linearity ( $R^2 = 0.979$ ) and yielded an  $E^{\circ}$  value of  $0.823 \text{ V}$  versus Ag/AgCl and an  $n$  value of

(14) Heineman, W. R. *J. Chem. Educ.* **1983**, *60*, 305–308.

(15) Skoog, D. A.; Holler, F. J.; Nieman, T. A. *Principles of Instrumental Analysis*, 5th ed.; Saunders: Philadelphia, 1998; p 338.

(16) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley-Interscience: New York, 1972; pp 860–861, 864.

(17) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, 1989.



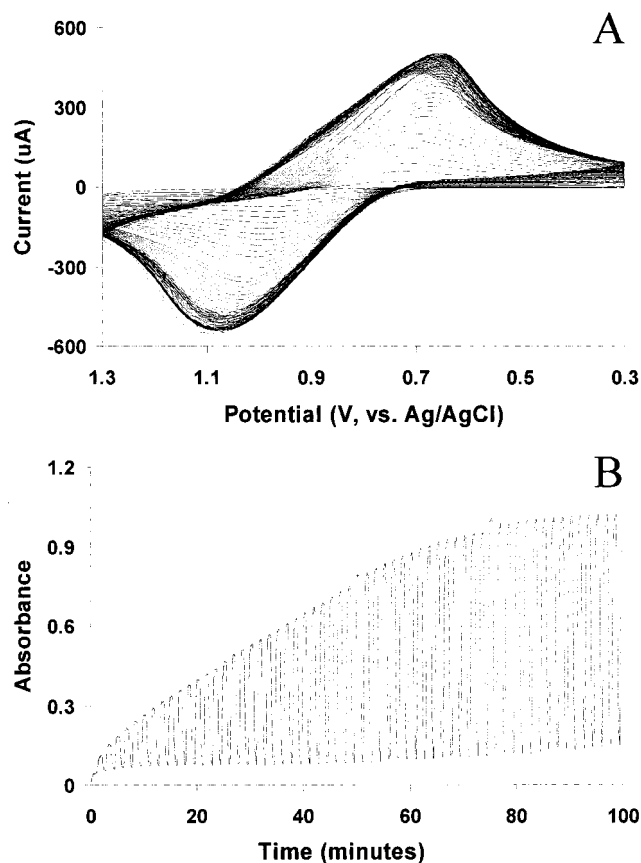


Figure 3. Panel A: series of cyclic voltammograms ( $v = 20$  mV/s) taken during uptake of  $\text{Fe}(\text{bipy})_3^{2+}$  from a solution of 0.1 mM  $\text{Fe}(\text{bipy})_3^{2+}$ , 0.1 M in NaCl by a Nafion-coated ITO OTE sensor. Panel B: optical modulation at 520 nm during incorporation of  $\text{Fe}(\text{bipy})_3^{2+}$  by a Nafion-coated ITO OTE sensor in ATR mode.

0.978. These values are in agreement with the reported  $E^\circ$  (0.898 V corrected to Ag/AgCl<sup>18</sup>) and the expected  $n$  value of unity and indicate that  $\text{Fe}(\text{bipy})_3^{2+}$  is well-behaved both electrochemically and optically at the ITO electrode.

**Partitioning of  $\text{Fe}(\text{bipy})_3^{2+}$  into a Cation-Selective Nafion Film.** Operation of the sensor relies on partitioning, retention, and stability of  $\text{Fe}(\text{bipy})_3^{2+}$  in the Nafion film, and this must also be evaluated. To this end, uptake of the complex ion into the Nafion-coated ITO electrode was evaluated both voltammetrically and spectroscopically using ATR. ATR offers two major advantages over the traditional transmittance experiment: (1) increased selectivity due to the minimal penetration of the evanescent wave, which probes only the contents of the film rather than the bulk solution, and (2) increased sensitivity due to the greatly increased optical path provided by the multiple reflections. Here, the cell was rinsed with electrolyte solution and then exposed to an aqueous solution of 0.1 mM  $\text{Fe}(\text{bipy})_3^{2+}$  and 0.1 M NaCl. Uptake of the complex ion by the film as a function of time is illustrated in Figure 3. Repetitive cycling at a potential sweep rate of 20 mV/s (panel A) indicates uptake and retention of the complex ion as shown by the increasing anodic and cathodic peak currents. The increase in the absorbance difference ( $\Delta A$ ) at 520 nm (panel B) with time further indicates the increasing concentration of

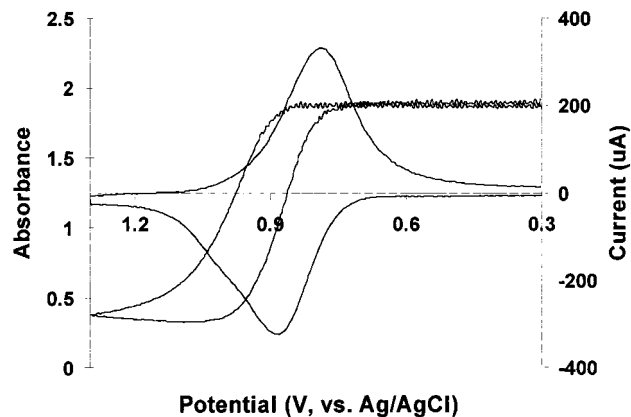


Figure 4. Cyclic voltammogram ( $v = 5$  mV/s) and corresponding change in absorbance for the same Nafion-coated ITO OTE sensor described in Figure 3 at equilibrium.

$\text{Fe}(\text{bipy})_3^{2+}$  accumulating in the film. That both peak current and  $\Delta A$  become constant at  $\sim 80$  min suggests that the partitioning of the complex ion into the film had reached equilibrium by that time.

The effectiveness of this sensor is further illustrated by the data in Figure 4, which shows a cyclic voltammogram of  $\text{Fe}(\text{bipy})_3^{2+}$  in the same film employed in Figure 3, but acquired at a slower scan rate of 5 mV/s after  $\text{Fe}(\text{bipy})_3^{2+}$  uptake had reached equilibrium. Overlaid on the voltammogram is the corresponding optical signal obtained as a function of time at 520 nm. It is apparent that there is direct correlation between electrochemical cycling of the complex ion in the film and the magnitude of the optical signal. All of these results taken together point toward the potential success of a Nafion-coated OTE as an effective sensor for  $\text{Fe}(\text{bipy})_3^{2+}$ . Of particular interest is the difference in the shape of the voltammetric waves between Figures 3 and 4, as well as the obvious difference in  $\Delta A$  once the iron uptake had reached equilibrium. These differences can be explained by the difference in the experimental time scale (voltammetric sweep rate) in each case. The voltammograms shown in Figure 3 (acquired at 20 mV/s) display typical diffusion-limited behavior, whereas the voltammogram shown in Figure 4 (acquired at 5 mV/s) is typical of a thin-layer voltammogram in which all of the electroactive species loaded into the film have been electrolyzed during the time scale of the potential sweep. Likewise, when the optical signal at equilibrium from Figure 3 is displayed as in Figure 4 (not shown), it does not flatten out during the course of a sweep cycle as it does in Figure 4. Both of these observations suggest that oxidation/reduction of the  $\text{Fe}(\text{bipy})_3^{2+}/^{3+}$  sequestered in the film is incomplete at a potential sweep rate of 20 mV/s whereas it is complete at 5 mV/s, thus explaining why  $\Delta A$  is larger in Figure 4 than at equilibrium in Figure 3.

**Performance of a Bipy-Loaded Nafion ITO OTE Sensor in the ATR Mode for Determination of Iron(II) in Pure Samples.** The uniqueness of the sensor design reported here is that it should be sensitive to free  $\text{Fe}^{2+}$  in solution; this is accomplished by preconcentrating the organic ligand into the charge-selective film prior to exposing the sensor to a sample solution containing aqueous iron ion. Our studies have indicated that a 2-h exposure of a Nafion film on an ITO electrode to a dilute solution ( $\sim 5$  mM) of bipy in either water or aqueous 0.1 M NaCl

(18) Harris, D. C. *Quantitative Chemical Analysis*, 5th ed.; W. H. Freeman: New York, 1999; p AP31.

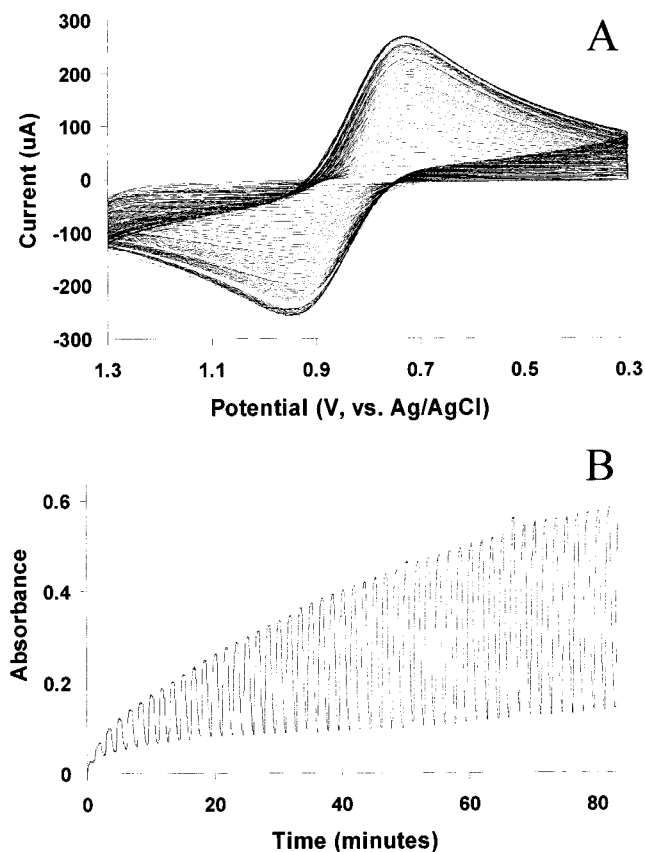
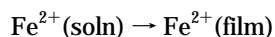


Figure 5. Panel A: series of cyclic voltammograms recorded with a Nafion-coated ITO OTE sensor that had been previously soaked in an aqueous solution that was 5 mM in bipy and 0.1 M in NaCl during uptake of  $\text{Fe}^{2+}$  from an aqueous solution of 0.1 mM  $\text{Fe}^{2+}$  and 0.1 M NaCl. The potential sweep rate was 20 mV/s. Panel B: optical modulation during uptake of  $\text{Fe}^{2+}$  by the sensor described in panel A.

results in uptake and retention of the free ligand in the film. This observation was verified by exposing the bipy-loaded film to an aqueous 0.1 mM solution of aqueous  $\text{Fe}^{2+}$  that was also 0.1 M in NaCl. Voltammograms were obtained as a function of time, and spectra were simultaneously acquired using both transmittance and ATR modes. Both the voltammograms and spectra were characteristic (via comparison of  $E^{\text{c}'}$  values and wavelength of maximum absorbance) of  $\text{Fe}(\text{bipy})_3^{2+}$  that formed as the free  $\text{Fe}^{2+}$  partitioned into the film and complexed with the preconcentrated ligand as described below.



A typical set of electrochemical and spectral data are shown in Figure 5, in which an ITO OTE in ATR mode was employed. Here, one can easily see the increase in both the peak current and  $\Delta A$  as  $\text{Fe}^{2+}$  partitions into the film, a process that is still continuing after 80 min as evidenced by the continuing increase in absorbance. Further data (not shown), however, indicate that the time required for the aqueous  $\text{Fe}^{2+}$  and the  $\text{Fe}(\text{bipy})_3^{2+}$  concentrations to reach equilibrium in the film is roughly comparable. We realize that such comparisons may be preliminary

at this point due to slight variations in film thickness between experiments. Such variations would be expected to have measurable effects on both the time required to reach uptake equilibrium and the measured magnitude of  $\Delta A$  due to increased capacity of a thicker film to accept more complex ion. An evaluation of the effect of potential sweep rate on peak current and  $\Delta A$  for  $\text{Fe}^{2+}$  in a bipy-preloaded Nafion film showed peak currents to increase with increasing sweep rate, producing a linear plot of peak current versus square root of potential sweep rate. This result indicates that the electrochemical conversion within the film is under semi-infinite diffusion control, which is consistent with the appearance of the cyclic voltammograms in Figure 5. The  $\Delta A$  values decrease with increasing sweep rate because less  $\text{Fe}(\text{bipy})_3^{2+}/\text{Fe}(\text{bipy})_3^{3+}$  (in the optical path, as defined by the evanescent wave penetration depth) is electrolyzed at the faster scan rates.

One concern that might be raised is that appreciable amounts of ligand could partition readily out of the film over the time frame of the experiment, leading to formation of the complex ion *outside* of the film, which may or may not re-enter the film and be detected. While we have up to this point been unable to quantitatively measure the degree to which ligand may be leaving the film, careful qualitative observation of films during single-pass transmittance measurements shows that while the films take on a distinct reddish color as the complex ion forms, the bulk solution remains colorless. This observation indicates that any leakage of the ligand out of the films (and subsequent combination with free  $\text{Fe}^{2+}$  in bulk solution) is minimal compared to the concentration that remains partitioned in the films.

Other permutations of this experiment were attempted as well. For example,  $\text{Fe}^{2+}$  was introduced first to the film, followed by ligand. In this case (data not shown), the voltammetry of the resulting complex was poorly defined, and  $\Delta A$  values were smaller than previously noted for like concentrations of  $\text{Fe}^{2+}$ . Furthermore, when transmittance experiments were attempted, the bulk solution took on a pale reddish tint, suggesting that either the  $\text{Fe}^{2+}$  or the complex ion was not strongly retained in the film.

Preliminary experiments involving incorporation of bipy into the Nafion film (by simple mixing) during the film preparation step were also attempted. While this approach showed some promise, opaque, nonrobust films resulted. It is possible that these problems could be mitigated in future work, as the prepared films employed very high concentrations of ligand in an effort to optimize optical signal strength.

The final goal of this work was to prove that the magnitude of the analytical signal ( $\Delta A$ ) of the sensor is proportional to the concentration of  $\text{Fe}^{2+}$  in aqueous solution. This task was fulfilled by comparing  $\Delta A$  values for analyte-saturated films exposed to solutions of varying  $\text{Fe}^{2+}$  concentration. Figure 6 is a compiled illustration of both the voltammetric and spectral responses of the sensor after exposure to solutions of 0.005 mM and 0.5 mM  $\text{Fe}^{2+}$ . Here, each measurement was acquired using a Nafion-coated ITO OTE in ATR mode; only data taken at equilibrated films are shown in each case. Each trial utilized a different film, so some variability in signal may exist due to small differences in film thickness. It is obvious that the larger solution concentration of  $\text{Fe}^{2+}$  leads to both larger voltammetric peak currents and greater optical response. These data indicate that the sensor response is indeed a function of solution analyte concentration. The detection

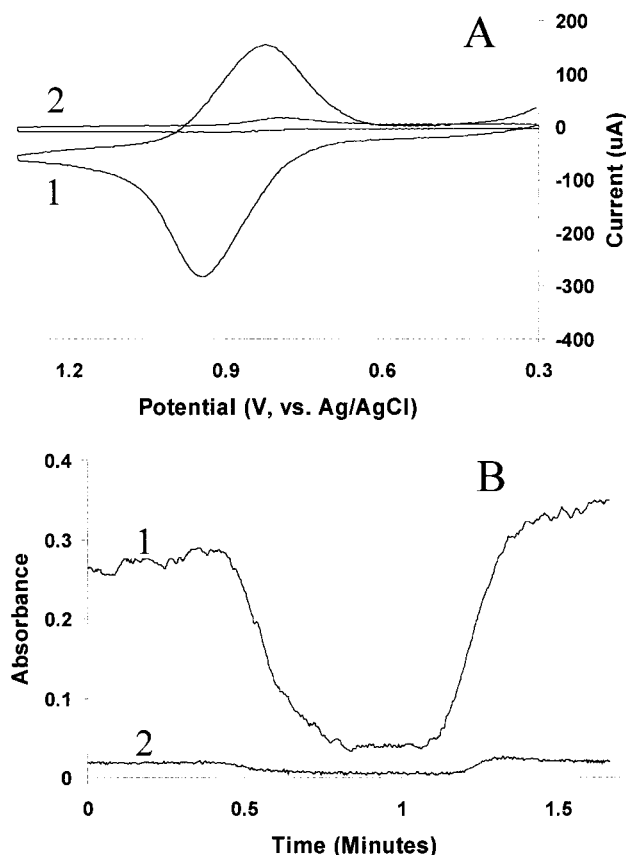


Figure 6. Results for the sensor described in Figure 5 exposed to two different concentrations of aqueous  $\text{Fe}^{2+}$  after soaking in aqueous 5 mM bipy/0.1 M NaCl for 2 h. Panel A depicts cyclic voltammograms recorded at 5 mV/s simultaneously with the absorbance changes shown in panel B. A1 and A2 correspond to the sensor exposures to 0.5 and 0.005 mM solutions of  $\text{Fe}^{2+}$ , respectively. B1 and B2 depict the changes in absorbance at 520 nm of the same sensor to 0.5 and 0.005 mM solutions of  $\text{Fe}^{2+}$ , respectively.

limit for this unoptimized sensor must fall below  $5 \times 10^{-6} \text{ M Fe}^{2+}$ , as a measurable  $\Delta A$  was obtained at this concentration. This number compares favorably with that reported earlier for a related ferricyanide sensor, which in its unoptimized form yielded a detection limit of  $8 \times 10^{-6} \text{ M Fe(CN)}_6^{3-}$ . As in this earlier sensor, we expect that detection limits can be lowered by employing signal averaging or optical waveguide technology. The upper concentration range should be related to the partition coefficient of the ligand into the Nafion film, which determines the concentration of ligand in the film available for complexation with  $\text{Fe}^{2+}$ .

## CONCLUSIONS

The results shown in this paper illustrate proof of concept for a spectroelectrochemical sensor for a metal ion that lacks the spectroscopic properties needed for this type of sensor by forming a strongly absorbing metal complex within the sensing film. Although demonstrated with aqueous  $\text{Fe}^{2+}$ , the concept is broadly applicable to many metals. Such a sensor should prove useful when soluble metal ions must be detected in remote-sensing

applications since the ligand required for complex ion formation needed to obtain optical sensitivity is preloaded into the charge-selective film. A sensor response related to analyte concentration has been established, and a preliminary detection limit for  $\text{Fe}^{2+}$  of 0.005 mM was achieved, though the useful concentration range of the sensor has not yet been determined.

In its present form, the sensor has a relatively slow response time to maximum sensitivity. The relationship between film thickness, response time, and sensitivity is under investigation. Thinner films give faster response, but sensitivity is compromised once the evanescent beam penetration depth exceeds the film thickness. However, in many environmental applications, response times on the order of 1 h are acceptable because only slow changes are being monitored. Also, measurements could be made more rapidly by not allowing the sensor to equilibrate with the sample, which is a commonly used method for speeding up measurements. The disadvantage is loss of sensitivity, which is not a problem for samples of sufficiently high concentration.

Future work with this sensor for  $\text{Fe}^{2+}$  will focus on understanding fundamental questions such as the partitioning properties of bipy into the Nafion film and the effect of bipy concentration in the film on sensor performance characteristics: linear range of the sensor response to analyte concentration, limit of detection, response time, reversibility, and ruggedness. Another focus will be the effect of metal ion interferences. As it is expected that metal cations besides iron could partition into the charge-selective film and form stable, colored complex ions with bipy, the effect of such interferences must be investigated. We would expect this interference to become most severe in cases where the formation constant of the complex ion formed by the interfering ion approaches or exceeds that of the  $\text{Fe(bipy)}_3^{2+}$  ion. Stable complexes of both the iron and the interfering agent could form. In such a case, selectivity based on differing electrochemical and optical properties would become important. Potentially interfering metal ions might include  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Hg}^{2+}$  as they have formation constants for  $\text{M}^{2+}(\text{bipy})_3$  near (or exceeding) that of  $\text{Fe}^{2+}$  in aqueous solution.<sup>17</sup> The effect of oxidation state of iron in the sample and the degree of selectivity provided by the ligand together with the charge-selective film and spectroelectrochemical modulation will be important in real applications. A better understanding of these issues will lead to optimization of sensor performance and eventual application of this sensor design.

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